PB88-124318

Interlaboratory Study of Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010 and Digestion Method 3050

Nevada Univ., Las Vegas

Prepared for

Environmental Monitoring Systems Lab.
Las Vegas, NV

Nov 87

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA/600/4-87/032

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE
AN INTERLABORATORY STUDY OF INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY METHOD 6010 AND DIGESTION METHOD 3050

5. REPORT DATE
November 1987

6. PERFORMING ORGANIZATION CODE
ERC

7. AUTHOR(S)
Clifton L. Jones, Vernon F. Hodge, Donald M. Schoengold, Homigol Biesiada, Thomas H. Starks, and Joseph E. Campana

8. PERFORMING ORGANIZATION REPORT NO.
QAL Report 157

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Environmental Research Center
University of Nevada, Las Vegas
Las Vegas, Nevada 89119-9770

10. PROGRAM ELEMENT NO.
D109

11. CONTRACT/GRANT NO.
Contract No. 68-01-7159

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Monitoring Systems Laboratory - LV, NV
Office of Research and Development
U.S. Environmental Protection Agency
Las Vegas, NV 89119

13. TYPE OF REPORT AND PERIOD COVERED
Project March 1986-April 1987

14. SPONSORING AGENCY CODE
EPA/600/07

15. SUPPLEMENTARY NOTES

Thomas A. Hinners, Project Officer

16. ABSTRACT

The design, execution, and results of an interlaboratory study of Method 6010, "Inductively Coupled Plasma Atomic Emission Spectroscopy," are described. The study examined the application of the method to the analysis of solid-waste materials for 23 elements. Part of the interlaboratory study included the study of Method 3050, "Acid Digestion of Sediments, Sludges and Soils," which is an integral part of Method 6010 when considering the analysis of certain solid wastes. The overall study was designed so that the variability of the two methods was separable. Method performance data, including precision and accuracy, are presented and discussed. A comparison of the inductively coupled plasma atomic emission and atomic absorption spectroscopic techniques is presented, as well as a comparison of results from two different types of inductively coupled plasma spectrometers. The limitations of the methods are described, and suggestions are given to improve the general application of Method 6010.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
222

22. PRICE

PB88-124318

EPA/600/4-87/032
November 1987

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Contract Number 68-01-7159
Contract Number 68-01-7253

Technical Monitor

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LAS VEGAS, NEVADA 89193-3478

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

NOTICE

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract Number 68-01-7159 to the University of Nevada, Las Vegas, Nevada, and under Contract Number 68-01-7253 to Viar and Company, Alexandria, Virginia. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The Quality Assurance Laboratory (QAL), a division of the University of Nevada, Las Vegas (UNLV) Environmental Research Center, was asked by the EPA Environmental Monitoring Systems Laboratory -- Las Vegas (EMSL/LV) to act as the coordinating laboratory for an interlaboratory study of EPA Method 6010. This project was assigned as one of the UNLV-QAL quality assurance support tasks under EPA Contract Number 68-01-7159. This Method 6010 project commenced in March 1986, and the modification and finalization of the experimental design was done in collaboration with the EPA EMSL/LV. Performance evaluation materials were shipped by the UNLV-QAL to the participating laboratories, under contract to the EPA, in June 1986 with an expected 30-day turnaround time. The UNLV-QAL review and audit and the completion of data packages by the participants for entry into the project data base were completed in mid-January 1987. This report is submitted in partial fulfillment of the responsibilities of the coordinating laboratory to provide a tabulation of the analytical results and a statistical evaluation.

The experimental design used in this study has resulted in several sets of multidimensional data. While this report satisfies the task requirements, the reader will observe that the data sets presented deserve much further consideration and evaluation. The authors suggest that further analysis and interpretation of this excellent data base be considered by the Agency because of the future application of the potential findings to metals analysis of solid wastes by inductively coupled plasma atomic emission spectroscopy.

ABSTRACT

The design, execution, and results of an interlaboratory study of Method 6010, "Inductively Coupled Plasma Atomic Emission Spectroscopy," are described. The study examined the application of the method to the analysis of solid-waste materials for 23 elements. Part of the interlaboratory study included the study of Method 3050, "Acid Digestion of Sediments, Sludges and Soils," which is an integral part of Method 6010 when considering the analysis of certain solid wastes. The overall study was designed so that the variability of the two methods was separable. Method performance data, including precision and accuracy, are presented and discussed. A comparison of the inductively coupled plasma atomic emission and atomic absorption spectroscopic techniques is presented, as well as a comparison of results from two different types of inductively coupled plasma spectrometers. The limitations of the methods are described, and suggestions are given to improve the general application of Method 6010.

This report was submitted in partial fulfillment of contract number 68-01-7159 by the University of Nevada, Las Vegas - Quality Assurance Laboratory under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from March 1986 to April 1987.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AAS	atomic absorption spectrometry
AES	atomic emission spectroscopy
CLP	EPA Superfund Contract Laboratory Program
CRDL	Contract Required Detection Level
EPA	U.S. Environmental Protection Agency
EPA-Cin	EPA Environmental Monitoring and Support Laboratory in Cincinnati
g	gram
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICV	initial calibration verification solution
ICS	interference check sample
IDL	instrumental detection limit
kg	kilogram
L	liter
LOD	limit of detection (3 x std dev)
LOQ	limit of quantitation (10 x std dev and 3.33 x LOD)
mg	milligram
nm	nanometers
MSA	method of standard additions
NBS	U.S. National Bureau of Standards
ND	not detected
percent RSD	percent relative standard deviation
ppb	parts per billion
ppm	parts per million
QA	quality assurance
QAL	Quality Assurance Laboratory (UNLV)
QC	quality control
RSD	relative standard deviation
SMO	Sample Management Office
SRM	Standard Reference Material (NBS)
UNLV	University of Nevada, Las Vegas
UNLV-QAL	University of Nevada, Las Vegas Quality Assurance Laboratory
ug	microgram

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AAS	atomic absorption spectrometry
AES	atomic emission spectroscopy
CLP	EPA Superfund Contract Laboratory Program
CRDL	Contract Required Detection Level
EPA	U.S. Environmental Protection Agency
EPA-Cin	EPA Environmental Monitoring and Support Laboratory in Cincinnati
g	gram
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICV	initial calibration verification solution
ICS	interference check sample
IDL	instrumental detection limit
kg	kilogram
L	liter
LOD	limit of detection (3 x std dev)
LOQ	limit of quantitation (10 x std dev and 3.33 x LOD)
mg	milligram
nm	nanometers
MSA	method of standard additions
NBS	U.S. National Bureau of Standards
ND	not detected
percent RSD	percent relative standard deviation
ppb	parts per billion
ppm	parts per million
QA	quality assurance
QAL	Quality Assurance Laboratory (UNLV)
QC	quality control
RSD	relative standard deviation
SMO	Sample Management Office
SRM	Standard Reference Material (NBS)
UNLV	University of Nevada, Las Vegas
UNLV-QAL	University of Nevada, Las Vegas Quality Assurance Laboratory
ug	microgram

SYMBOLS

Al	aluminum
Ag	silver
AgCl	silver chloride
As	arsenic
B	Boron
Ba	barium
Be	beryllium
Ca	calcium
Cd	cadmium
Co	cobalt
Cr	chromium
Cu	copper
Fe	iron
K	potassium
Mg	magnesium
Mn	manganese
Mo	molybdenum
Na	sodium
Ni	nickel
Pb	lead
Se	selenium
Sb	antimony
Si	silicon
Tl	thallium
V	vanadium
Zn	zinc

ACKNOWLEDGMENTS

Thomas A. Hinners, the EPA Task Monitor (Environmental Monitoring Systems Laboratory - Las Vegas), is thanked for his guidance and assistance in the execution of this project. Use of the EPA contracts numbered 68-01-7159 and 68-01-7253 for this study was graciously permitted by the respective project officers, Duane A. Geuder and Michael H. Carter. Special thanks also go to the participating laboratories, especially Cheryl Daniel (Centec Analytical Services), Edward Dantsker (JTC Environmental Consultants, Inc.), Robert K. Patel (Lockheed Engineering and Management Services Co.), Kenneth Erondu (Spectrix Corp.), William Nivens (Versar, Inc.), Bernadine Siemens (Wilson Laboratories), Gail Solomon (Hittman-Ebasco Associates, Inc.), and Steven Vincent (Weyerhaeuser Company). We thank Edward Berg (EPA Environmental Monitoring and Support Laboratory - Cincinnati) for supplying three of the solid waste materials used in this study.

INTRODUCTION

An interlaboratory study of solid wastes using the EPA analytical Method 6010 entitled "Inductively Coupled Plasma Atomic Emission Spectroscopy" (ICP-AES) [Appendix A], which is included in the EPA methods publication SW-846 (1), was performed with 9 participating laboratories. This interlaboratory study concentrated on the application of Method 6010 for the determination of 23 elements in solutions that were derived from seven solid materials including dried sludges, sediments, and fly ash. The 23 target elements are: Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, K, Pb, Mg, Mn, Mo, Ni, Se, Ag, Na, Tl, V, and Zn. This study followed a single-laboratory evaluation that investigated the application of Method 6010 to a variety of aqueous and solid-waste samples (2). The different waste matrices studied in the single-laboratory evaluation required the utilization of several different digestion procedures (2). In contrast, this interlaboratory study examined Method 6010 for the analysis of solid wastes that were digested using a single digestion procedure.

Since the digestion of solid samples is necessary to apply Method 6010 for the analysis of wastes, a thorough study of Method 6010 must also include digestion as a variable. Consequently, a parallel study of Method 3050 (Acid Digestion of Sediments, Sludges, and Soils) [Appendix B] was included as an integral part of the interlaboratory study. The present study was designed to determine the performance of Method 6010 both independent of and together with the Method 3050 digestion procedure.

Seven solid materials, representative of solid wastes, were selected as the method evaluation materials. Three of the materials (river sediment, coal fly ash, and estuarine sediment) are Standard Reference Materials from the National Bureau of Standards, and one material (the mine tailing) is an EPA reference material. The other three solids (a contaminated soil and two industrial sludges) were obtained from the EPA. A detailed homogeneity study was performed by the coordinating laboratory before the solids were distributed to the participating laboratories [Appendix C]. The results indicated that the solid samples were homogeneous.

Sixteen grams of these homogeneous solids were distributed to the laboratories to be digested by Method 3050, both unspiked and spiked, and analyzed by Method 6010. The spiking solutions that were provided to the laboratories contained 19 of the 23 target elements. They were designed to be added to the solids prior to digestion in order to bring the concentrations of the 19 elements in the laboratories' digests to minimum levels of about 100 times the corresponding "Estimated Instrumental Detection Limits" given in Method 6010. It was not necessary to spike Al, Ca, Fe, and Mg into the solids because of the high endogenous concentrations of these metals in the 7 solid samples. Having each laboratory spike portions of the solid samples with the spiking solutions prior to digestion assured that each laboratory used equally spiked aliquots of the solids. This procedure eliminated the need to create uniformly spiked solids for distribution.

In order to remove sample-preparation variability from measurement variability, bulk digests of the 7 solid samples were prepared by the coordinating laboratory for distribution to the participating laboratories. These bulk digests were spiked with the same spiking solutions that were used to spike the solid samples. This procedure yielded a solution in which the concentrations of all of the 23 elements were about 100 times the corresponding "Estimated Instrumental Detection Limits." Thus, the spiked bulk digests were very similar in composition to the spiked solids digests that were prepared by the participating laboratories. Therefore, data from the Method 6010 analyses of these spiked bulk digests could be compared to data from the spiked solids in order to estimate the variances due to the digestion and analysis procedures. In order to test the effects of high levels of V and Mo on the determination of the other analytes by Method 6010, the spiked bulk digest from the fly ash solid was also spiked to contain 0.1 percent of these interfering elements.

In addition to the solid samples and the spiked bulk digests, two QC solutions containing the target elements were provided to the participating laboratories for analysis with and without digestion. Because these solutions were carefully prepared and verified by the coordinating laboratory, the results could be used to estimate the accuracy of the Methods. Other solutions were provided to the participating laboratories to assure high ICP-AES data quality. These were initial calibration verification solutions and an interference check solution.

The results of this collaborative study yielded quantitative information on the precision and accuracy of Method 6010, independently and together with Method 3050. Data obtained on sequential and simultaneous ICP-AES instruments as well as by atomic absorption spectroscopy (AAS) were compared statistically, and the results are reported. The method of standard additions (MSA) is a conditional requirement of Method 6010, so its effect on data quality was investigated.

SECTION 2

SUMMARY AND CONCLUSIONS

This multilaboratory evaluation of Method 6010 demonstrates that the method, as described, is capable of achieving excellent accuracy and precision for the determination of the 23 elements in quality control (QC) solutions. These QC solutions contained the 23 elements at concentrations of approximately 100 times the instrumental detection limits, and the solutions were interference-free in that no interfering elements were present at high concentrations. Accuracies for the determination of the 23 elements in the QC solutions (when the mean reported values are expressed as a percentage of the target or "true" values) vary from 95 percent to 104 percent for the solutions that were analyzed without digestion and vary from 93 percent to 103 percent (silver excluded) for the solutions that were digested before analysis. Digestion of the QC solution containing silver resulted in a mean silver value that is only 53 percent of the target value whereas the mean silver value is 100 percent of the target value for the direct analysis of this QC solution. The percent RSD's, which are a measurement of precision, range from 3.1 percent to 9.1 percent for the 23 elements in the QC solutions that were analyzed by Method 6010 without digestion and from 2.6 percent to 13 percent (when silver is excluded) for the QC solutions that were analyzed after digestion by Method 3050. The median percent RSD's, across the 23 elements, for the 2 sets of QC solutions are 6.5 percent and 6.7 percent, respectively. These precisions are considered excellent. Silver with a percent RSD of 52 percent is the lone outlier in the QC solution set that was digested before analysis.

The interlaboratory precision for Method 6010, with digestion eliminated as a variable, was determined for the 23 elements in the spiked bulk digests of 6 representative solid complex matrices, including river and estuarine sediments and industrial sludges. The analyte concentrations in these spiked bulk digests were about 100 times the instrumental detection limits. The median percent RSD's for the 6 sediments, across the 23 elements, range from 6.8 percent to 11 percent. Thus, the precision for the measurement of the target elements in these complex solutions is very good.

The seventh spiked bulk digest, from coal fly ash, was spiked with very high levels of molybdenum and vanadium (0.1

percent). The median percent RSD's for the determination of the 23 elements in this spiked bulk digest range from 4.2 percent to 83 percent with a median of 16 percent. An analysis of the data suggests that these two elements decreased the measurement precision of many of the target elements.

When Method 6010 and Method 3050 are applied in combination for the determination of the 23 elements in the spiked solids, the apparent measurement precision decreases when compared to the corresponding spiked bulk digest. The median percent RSD's for the 7 solids across the 23 elements range from 11-18 percent. The spiked solid samples were spiked prior to digestion to assure that the concentrations of the analytes in the resulting digests were approximately 100 times greater than the instrumental detection limits.

The median percent RSD's for the same 7 solids, unspiked, range from 17-27 percent. This poorer precision when compared to the spiked solids results because over 50 percent of the reported concentration values in the unspiked solids are less than 100 times the average of the instrumental detection limits. In other words, as the concentrations approach the instrumental detection limits the precision decreases as indicated by the higher percent RSD values. Four elements among those with the highest median percent RSD's are antimony, arsenic, selenium, and silver. For the major elements that were present in the digests of the unspiked solids at concentrations 100 times greater than the IDL's (due to their occurrence in high concentrations in the unspiked solids), the precision is comparable to the precision for the spiked solid samples.

The Method 6010 variance and the Method 3050 variance can be calculated from the data base resulting from the analyses of the spiked bulk digests and the spiked solid samples. A statistical analysis of the data shows that in general, the digestion procedure and the ICP-AES analytical procedure contribute about equally to the overall measurement uncertainty or precision (variance) for the determinations of the 23 target elements in digests of these 7 homogeneous solids.

The accuracy of the ICP Method 6010 can be estimated for these complex matrices by comparing the mean concentrations of the elements in the spiked bulk digests (as determined by Method 6010) to the corresponding concentrations which were determined by AAS by one of the participating laboratories. A null hypothesis approach that is based on the mean and on the corresponding standard deviation was used to determine if the ICP-AES and AAS values are significantly different at the 95 percent confidence level. The results indicate that only two out of 184 elemental measurements by the two methods are significantly different. The ICP-AES mean value was statistically higher than the AAS value for Ca in the digests of the Estuarine Sediment and the Mine Tailing Waste. In some cases where the ICP/AAS ratios are very different (less than 0.75 or greater than 1.25), the standard deviations in the ICP measurements are very high, and, therefore, the differences in the means are not significant. Overall, the agreement between ICP and AAS is excellent.

The method of standard additions was required for less than 10 percent of the total analyses. Results by ICP-AES using the method of standard additions were compared with non-MSA data for the spiked bulk digest samples. The comparison of this limited data set indicates that on the average there is no consistent improvement in the data quality when the method of standard additions is used with Method 6010 for the analysis of the 7 solid matrices that were used in this study.

A comparison between data obtained on simultaneous and sequential inductively coupled plasma spectrometers indicated that the concentration values were statistically indistinguishable.

SECTION 3

RECOMMENDATIONS

The experimental design used in this multilaboratory study has resulted in several excellent sets of multidimensional analytical data that deserve consideration beyond the intended scope of this report. Further analysis and interpretation of this data base is suggested.

The presence of high concentrations (0.1 percent) of vanadium and molybdenum in the fly ash spiked bulk digest could account for the apparent decrease in the measurement precision of many of the 23 target elements in this matrix compared to the 6 other spiked bulk digests. The interfering effects in this matrix should be studied further.

The poor precision, accuracy, and spike recoveries for silver demonstrated in this study, should be noted in both Method 3050 and Method 6010. The possibility of precipitation in the nitric/hydrochloric acid digestion matrix as well as phototransformation should be discussed in Method 3050.

The poor spike recovery of antimony, observed in this study, should be noted in Method 3050. In particular, the possibility of the formation of oxide and oxo-chloride precipitates of antimony in the nitric/hydrochloric acid digestion matrix should be discussed.

The application of the method of standard additions (MSA), a conditional requirement of Method 6010, affects the economics, the turnaround time of analysis, the practicality of the Method, as well as the data quality. Although this report indicates that, on the average, MSA data were not consistently different from non-MSA data, the requirement for the application of the MSA should be investigated further.

When soil-containing matrices are being analyzed by Method 6010, the authors are of the opinion that the method of standard additions should not be required for those elements that are endogenous to soils in high concentrations. The high-concentration endogenous elements in soils include Al, Ca, Fe, and Mg.

Required detection limits should be included in Method 6010 to assure uniform limits of detection. Recommended required detection limits, based on this interlaboratory study, are presented in this report.

Methods 6010 and 3050 should be reviewed carefully for technical completeness and comprehensiveness in view of the findings and experience obtained in this multilaboratory evaluation.

SECTION 4

EXPERIMENTAL DESIGN

The objectives of this multilaboratory study were to extend the single-laboratory evaluation (2) and to determine the full method performance of an EPA inductively coupled plasma atomic emission spectroscopy (ICP-AES) method that is used for the determination of metals in solution. This method is known as Method 6010 and is given in Appendix A. It is applicable to 25 metals that may be present in various matrices that require acid digestion prior to analysis, such as groundwater, aqueous wastes, soils, sludges, sediments, and other solid wastes. The metals are: Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, K, Pb, Mg, Mn, Mo, Ni, Se, Si, Ag, Na, Tl, V, and Zn. Because dissolved solids can have an adverse effect on the accuracy of the spectroscopic determinations of these metals, 7 solid wastes that represent typical waste matrices were chosen for the interlaboratory validation study. These solids were chosen with the expectation that the method performance based on their analysis would represent a worst case.

The analytical results for solid waste materials are dependent on the digestion method used to solubilize the analytes in solid materials, as well as on the spectroscopic measurement method. Therefore, in order to perform a complete method performance study, a digestion procedure, recommended for solid-type wastes, was also evaluated in this study; Method 3050, "Acid Digestion of Sediments, Sludges, and Soils," was chosen. This digestion Method is given in Appendix B, and it is applicable to 23 of the 25 elements specified in Method 6010 (boron and silicon were excluded).

The interlaboratory study was designed to determine the performance of Method 6010 both independent of and together with the Method 3050 digestion procedure. The study examined the determination of 23 elements by ICP-AES in 7 sediment, sludge, and soil waste samples by 9 laboratories.

PERFORMANCE EVALUATION MATERIALS

The Method 6010 performance was evaluated through the multilaboratory analysis of blind solutions. The performance of Method 6010 with the digestion Method 3050, herein referred to as Method 3050/6010, was evaluated through the multilaboratory analysis of blind homogeneous solids (sediments, sludges, and soils). Moreover, it was decided to derive Method 6010 performance evaluation solutions from the 7 Method 3050/6010 performance evaluation solids.

A list of all of the materials that were sent to the laboratories and that are discussed below is given in coded form in Table 1 of Appendix D.

Method 3050/6010 Performance Evaluation Materials

Seven solid materials, representative of typical solid wastes, were selected as the Method 3050/6010 performance evaluation materials. These materials and their sources are listed in Table 1. The first four solids in Table 1 are well characterized. The first three (river sediment, coal fly ash, and estuarine sediment) are Standard Reference Materials from the National Bureau of Standards. The fourth material (mine tailing) is a SUPERFUND Contract Laboratory Program (CLP) reference material that was designed and prepared by the University of Nevada, Las Vegas Quality Assurance Laboratory (UNLV-QAL). The elemental composition of this material was determined previously in a multilaboratory referee analysis using CLP analytical procedures. The last three materials (a contaminated soil and industrial sludges) were obtained from the EPA Environmental Monitoring and Support Laboratory in Cincinnati (EPA-Cin) for which no analytical data were provided.

In order to assure the homogeneity of all of these performance evaluation solids, a detailed, statistically-valid homogeneity study was designed and performed by the coordinating laboratory. The results of the homogeneity study are described in Appendix C. A statistical analysis of the analytical results indicated that the solids were homogeneous.

Duplicate Method 3050/6010 Digestions--

The participating laboratories were provided with more than 16 grams of each of the Method 3050/6010 solids. Two 4-g portions were designated for duplicate (unspiked) digestions, one of which was to be used also for a percent solids determination. The two remaining 4-g portions were designated for duplicate spiked digestions using the blind spiking solutions described below. The details of these procedures can be found in the Supplemental Instructions [Appendix D] and in the Participating Laboratories Statement-of-Work [Appendix E]. The participating laboratories were required to report the percent solids for the 7 Method 3050/6010 solids.

TABLE 1. THE SEVEN METHOD 3050/6010 PERFORMANCE EVALUATION SOLIDS*

Description	Source
River Sediment	NBS-SRM 1645
Coal Fly Ash	NBS-SRM 1633a
Estuarine Sediment	NBS-SRM 1646
Mine Tailing	UNLV-QAL
Hazardous Waste 1	EPA-Cin
Industrial Sludge	EPA-Cin
Electroplating Sludge	EPA-Cin

* These 7 solids were used to measure the performance of Method 6010 with the digestion Method 3050. These same 7 solids were also used to prepare the 7 Method 6010 performance evaluation solutions (spiked bulk digests of the 7 solids), that were used to measure the performance of Method 6010 independently of Method 3050.

It is important to note here that Method 3050 was modified appropriately to allow for the digestion of four grams of material rather than the specified 1-to-2 gram portion. This was done by simply doubling the quantities of all of the reagents. This modification was necessary because the standard Method 3050 procedure produces 100 mL of digest, and this quantity is insufficient if a sequential ICP spectrometer is used with Method 6010 and if the method of standard additions is applied. The larger quantity of solid (two grams rather than one gram, or when doubled, four grams rather than two grams) was chosen to maximize dissolved solids, matrix effects, and interferences. In other words, the larger portion was chosen as a worst case in order to challenge Method 6010.

Blind Spiking Solutions--

Theoretically, each of the 7 Method 3050/6010 solids could contain the 23 elements of interest in concentrations that vary from less than the IDL to several hundred times greater than the IDL. Therefore, in order to evaluate the method performance with respect to each element, it was necessary to assure that the concentration of each element was significantly above the IDL. This was accomplished by the production of a blind pair of stable spiking solutions by the coordinating laboratory.

The spiking solutions that were provided to the laboratories contained 19 of the 23 target elements. They were designed to be added to the solids prior to digestions in order to bring the concentrations of the 19 elements in the laboratories' digests to minimum levels of about 100 times the corresponding "Estimated Instrumental Detection Limits" given in Method 6010. The four geochemically endogenous elements, Al, Ca, Fe, and Mg were not included in the spiking solutions because it was expected that these four elements would be present in the 7 solid materials in sufficiently high concentrations. The spiking solutions were prepared from a series of custom standard solutions (SPEX Industries Inc., Edison, NJ). Two solutions were used because of the practical limitations imposed on preparing a stable solution containing all 23 target elements at relatively high concentrations from the standard solutions that were commercially available. Spiking a weighed portion of each of the 7 solids with these spiking solutions prior to digestion assured that a sufficient level of each of the 23 elements was present in the resulting digestate and that each laboratory used equally spiked aliquotes of the 7 solids. This procedure eliminated the need to create uniformly spiked solids for distribution. The expected nominal concentrations of the 23 target elements in the spiked solids are found in Table 2.

TABLE 2. MINIMUM CONCENTRATION OF ELEMENTS RESULTING FROM SPIKING THE PERFORMANCE EVALUATION MATERIALS

Element	Method 6010 Spiked Bulk Digests (µg/L)	Method 3050/6010 Spiked Solids (mg/kg)	Factor Above the Minimum Average IDL[a]
Al	-*	-*	-
Sb	5000	250	71
As	5000	250	36
Be	1000	50	416
Cd	1000	50	156
Ca	-*	-*	-
Cr	1000	50	91
Co	1000	50	63
Cu	1000	50	91
Fe	-*	-*	-
Pb	5000	250	56
Mg	-*	-*	-
Mn	1000	50	232
Mo	1000#	50	45
Ni	1000	50	50
Se	8000	400	40
Ag	1000	50	37
Tl	5000	250	28
V	1000#	50	43
Zn	1000	50	111
Ba	1000	80	77
Na	20000	1000	22
K	20000	1000	16

[a] The average IDL was computed from the IDL reported by each participating laboratory.

* High concentrations of these elements are endogenous to Method 3050/6010 solids; therefore, they were not added.

# Spiked bulk digest from the fly ash solid was also spiked to contain 1,000,000 µg/L (0.1 percent) of Mo and V.

Method 6010 Performance Evaluation Solutions- The Spiked Bulk Digests

The Method 6010 performance evaluation solutions were prepared by the coordinating laboratory by digesting 40 grams of each of the materials listed in Table 1 according to Method 3050 (reagent quantities appropriately adjusted). These bulk digests were filtered as necessary to remove suspended solids and they were spiked with the same spiking solutions that were provided to the participating laboratories to spike the 7 performance evaluations solids. Therefore, the spiked bulk digests prepared by the coordinating laboratory for the evaluation of Method 6010 were designed to be nearly identical in composition to the spiked solids digests that the individual laboratories prepared. Thus, uncertainties in the analyses of the spiked bulk digests are due to interlaboratory differences in the Method 6010 spectroscopic determination while the uncertainties in the Method 3050/6010 analyses of the spiked solids are due to variances both in the digestion and spectroscopic measurement procedures. The expected nominal concentration of the 23 target elements in the spiked bulk digests are found in Table 2.

For the accurate spectroscopic determination of the 23 target elements it is imperative that appropriate ICP-spectrometer correction factors be applied by the ICP system in order to compensate for interelement interferences. In order to test the effect of some specific interferences on the quantification, one of the Method 6010 spiked bulk digests, based on coal fly ash (NBS-SRM 1633a), was spiked additionally with high levels of vanadium and molybdenum (0.1 percent).

The stability of all the spiked bulk digests was monitored over time to demonstrate that the elemental concentrations did not change significantly during the study period. The excellent interlaboratory results (discussed below) also attest to their stability.

QUALITY ASSURANCE/QUALITY CONTROL

Several types of additional samples were designed and provided to the participating laboratories to assure high data quality. These included blind QC solutions, known initial calibration verification solutions, and a known interference check solution. Other QC requirements, including the analysis of blanks, are discussed in Method 6010 [Appendix A]. All of the data packages from the participating laboratories were audited for contract and method compliance, and corrective action was required, where practical, in order to maximize the useful data. Participating laboratories with experience in the CLP were chosen, because it was expected that CLP QA/QC procedures and good laboratory practices would be followed. (A list of the QC materials discussed below is given in coded Table 1 of Appendix D.)

Blind Quality Control Solutions

Two blind QC solution sets, which were free from high levels of interfering elements, were designed for the study. They were prepared quantitatively from high purity custom standard solutions (SPEX Industries Inc., Edison, NJ). One solution of each set contained 20 elements: Al, Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mo, Ni, Se, V, Zn, Ba, Na, K, and the other solution contained Mn, Ag, and Tl. Two solutions were necessary for each set because of the impracticality of preparing a single stable solution from the available standard solutions. The concentrations of the elements in the solutions were at least 100 times the estimated instrumental detection limits (IDL's).

Method 6010 Blind QC Solutions--

One of the QC solution sets was provided to the participating laboratories with the 7 Method 6010 spiked bulk digests. In other words, the participating laboratories received 9 Method 6010 performance evaluation solutions, two of which were the blind interference-free QC solutions.

Method 3050/6010 Blind QC Solutions--

A second QC solution set was provided to the participating laboratories to be processed and analyzed with the 7 Method 3050/6010 performance evaluation solids. These blind QC solutions were to be digested without spiking.

Calibration QC Solutions

As part of the QA/QC program, the coordinating laboratory provided the participating laboratories with four initial calibration verification solutions and an interference check solution. These reference solutions were designed and produced by the UNLV-QAL in support of the CLP, and the participating laboratories received the "true" values of the elemental composition that were determined by an EPA-conducted referee analysis. The four initial calibration verification solutions allowed the participating laboratories to verify independently the calibration of their ICP spectrometer. The participating laboratories were required to analyze these solutions at least once after each calibration of the ICP spectrometer and to be within ± 10 percent of the "true" concentration values. According to Method 6010 (Section 7.63), the interference check solution must be used to verify the interelement correction every 20 samples. The control limits for the interference check solution are ± 20 percent of the "true" values of the elemental composition. Further details on the use of these solutions can be found in Method 6010 and in the Method 6010 Supplemental Instructions [Appendix D]. The data sheets on these calibration solutions can be found in Attachment 1 of Appendix D.

Data Audits

Reporting Requirements--

The participating laboratories were required to report their data on standard CLP Inorganic Data Forms which were modified as necessary for Method 6010. These forms are provided in Appendix D, the Supplemental Instructions. The participating laboratories were given 30 days to submit complete data packages to the coordinating laboratory.

Compliance Audits--

Audits of the data-packages were conducted in two phases. The first audit was to check that all deliverables were included in the data packages. The coordinating laboratory requested corrective action through the EPA on all deficiencies in reporting requirements. Once all the deliverables were received, a second computer-aided audit was implemented to check that all the criteria of the QA/QC parameters were satisfied. The coordinating laboratory requested corrective action through the EPA on all deficiencies that affected data quality.

PARTICIPATING LABORATORIES AND INSTRUMENTATION

The participating laboratories were selected by representatives of the EPA and by the Sample Management Office [SMO] of the EPA (Viar, Inc.) on the basis of the bids the laboratories submitted in response to the Participating Laboratories Statement-of-Work [Appendix E] provided by the EPA. Seven laboratories with experience in the EPA CLP program were chosen, and the two EPA CLP referee laboratories were assigned to participate in the interlaboratory study. The nine participating laboratories are listed in Table 3, and Table 4 lists the manufacturer and model of the ICP spectrometers that the laboratories used. It was planned to obtain method performance data on equal numbers of simultaneous and sequential ICP spectrometers; however, only a few of the laboratories that responded with a bid had simultaneous instruments. One of the participating laboratories also provided atomic absorption spectroscopy analytical data for the spiked bulk digests.

The participating laboratories were provided with copies of Method 6010 [Appendix A], Method 3050 [Appendix B], and a Participating Laboratory Statement-of-Work [Appendix E] through

TABLE 3. PARTICIPATING LABORATORIES

EPA CLP Laboratories

Centec Analytical Services
Salem, VA

Hittman-Ebasco Associates, Inc.
Columbia, MD

JTC Environmental Consultants, Inc.
Rockville, MD

Spectrix Corp.
Houston, TX

Wilson Laboratories
Salina, KS

Versar Inc.
Springfield, VA

Weyerhaeuser Company
Federal Way, WA

EPA CLP Referee Laboratories

Lockheed Engineering and Management Services, Co.
Las Vegas, NV

University of Nevada/Environmental Research Center
Las Vegas, NV

TABLE 4. ICP SPECTROMETERS USED IN THE INTERLABORATORY STUDY

Manufacturer and Model
Perkin-Elmer Plasma II*
Perkin-Elmer 6500*
Perkin-Elmer 6000
Applied Research Laboratory 34000
Applied Research Laboratory 35000
Jarrell-Ash 115 (simultaneous)
Jarrell-Ash 975 (simultaneous)

* Two of the participating laboratories used these instruments.

the SMO. The Coordinating Laboratory, which designed and prepared the variety of samples used in this study, prepared a document entitled "Method 6010 Interlaboratory Study Sample Description, Procedures, and Supplemental Instructions" and provided the document to the participating laboratories in the shipment of the performance evaluation samples. This supplemental document was necessary because of the variety of coded (blind) samples and the need to clarify some sections of the Statement-of-Work. This supplemental document is included as Appendix D of this report.

COORDINATING LABORATORY

The coordinating laboratory for this study was the Quality Assurance Laboratory (QAL), a division of the University of Nevada, Las Vegas (UNLV) Environmental Research Center. This laboratory serves as an EPA CLP Referee Laboratory. The UNLV-QAL also participated in this study in that the same samples provided to the other participating laboratories were analyzed, and the analytical results were used to evaluate the Method 3050/6010 and Method 6010 performance. The Coordinating Laboratory Statement-of-Work is included as Appendix F.

SECTION 5

RESULTS

This section presents the results of the interlaboratory determination of the 23 target elements in

a. the 9 Method 6010 performance evaluation solutions, which include 7 spiked bulk digests and 2 blind QC solutions, and

b. the 7 duplicate spiked and unspiked Method 3050/6010 performance evaluaition solids and the 2 corresponding blind QC solutions.

All analytical values are reported in units of ug/L (ppb) for the Method 6010 spiked bulk digests and the QC solutions, and they are reported in units of mg/kg (ppm) for the Method 3050/6010 spiked and unspiked solids. The relevant data from the laboratories are presented in Tables 5 through 11. The experimental data from the participating laboratories is presented exactly as it was reported. The statistics presented in the tables were calculated with the outliers and not detected measurements excluded. The outliers, which are underlined in the tables, were determined by Grubbs Test (3) at the 95 percent probability level. The standard deviation values are reported to 2 significant figures following the guidance of the Association of Official Analytical Chemists (8).

DETECTION LIMITS

Table 5A lists the instrumental detection limits that each participating laboratory reported for each of the 23 target elements along with the corresponding spectral wavelength. Recommended wavelengths are given in Table 1 of Method 6010 [see Appendix A]. The limit of detection (LOD) and limit of quantitation (LOQ) values are given in Table 5B. The LOD is the IDL value (Table 5A) expressed in mg/kg for solids (adjusted for the dilution factor of 50 when 4-g are digested to yield 200 mL of solution). The LOQ is 3.33 times the LOD when the LOQ is derived from 10 times the standard deviation of the instrumental noise level and the LOD is derived from 3 times the standard deviation of the noise (8).

TABLE 5A. INSTRUMENTAL DETECTION LIMITS (IDLs) REPORTED AND WAVELENGTHS USED BY THE PARTICIPATING LABORATORIES

	LABORATORY																	
	A		B		C		D		E		F		G		H		I	
ELEMENT	IDL[a]	Wave-length[b]	IDL[a]	Wave-length[b]	IDL[a]	Wave-length[b]	IDL[a]	Wave-length[b]	IDL[a]	Wave-length[b]	IDL[a]	Wave-length[b]	IDL[a]	Wave-length[b]	IDL[a]	Wave-length[b]	IDL[a]	Wave-length[b]
Al	118	308.215	88.3	308	184	308.215	21	396.162	192	308.215	32	308.215	17	308.2	100	308	160	237.335
Sb	45	206.838	35.4	206	84	206.833	70	217.581	116	206.833	93	206.833	25	217.5	100	218	60	206.833
As	135	193.766	58.3	193	111	193.696	400	189.042	92	193.696	200	193.696	22	193.6	30	194	200	193.696
Be	4	313.043	3	313	2.5	313.042	1	234.861	3	313.042	1	313.042	1	313	3	313	3	313.042
Cd	4	214.438	4.8	226	4.6	214.438	10	214.438	4	226.502	18	226.502	4	328.8	3	229	5	214.438
Ca	93	317.933	9.6	317	940	317.933	15	317.933	280	317.933	5	317.933	4	317.9	70	318	4500	422.673
Cr	8	205.563	6.4	267	8.7	267.716	31	205.552	9	267.716	7	267.716	4	267.7	13	268	10	205.552
Co	16	228.616	6.8	228	23	228.616	12	228.616	30	228.616	11	228.616	4	228.6	4	229	38	228.616
Cu	16	324.753	6	324	24	324.754	10	224.7	10	324.754	3	324.754	3	324.7	13	325	17	324.754
Fe	10	259.94	6.8	259	73	259.94	10	238.204	60	259.94	8	259.94	3	259.9	20	260	80	259.94
Pb	10	220.353	53.6	220	67	220.353	71	220.353	124	220.353	62	220.353	35	220.3	200	220	180	220.353
Mg	238	279.079	7.7	285	720	279.079	2	279.553	310	383.826	25	279.079	1	279.5	20	280	3600	285.213
Mn	3	257.615	3.1	257	12	257.61	2	257.61	4	257.61	1	257.61	1	257.6	2	258	11	257.61
Mo	30	202.03	10.5	202	15	202.03	60	203.844	17	202.03	16	202.03	4	202	6	202	30	202.03
Ni	20	231.605	10	231	27	231.604	17	231.604	23	231.604	20	231.604	8	231.6	20	232	31	231.604
Se	292	196.096	83	196	162	196.026	200	196.09	126	196.026	220	196.026	41	196	100	196	590	196.026
Ag	10	328.068	15.9	328	14	328.068	4	328.068	8	328.068	6	328.068	3	328	10	328	20	328.068
Tl	181	190.864	79	190	116	190.864	400	190.864	84	190.864	189	190.864	49	190.8	200	352	300	190.864
V	21	292.4	5.8	292	19	292.402	50	292.402	17	292.402	5	292.402	50	292.4	3	292	35	292.402
Zn	12	213.856	3.1	213	18	213.856	12	213.856	9	213.856	4	213.856	2	213.8	3	214	17	213.856
Ba	5	455.4	4.1	455	17	233.527	3	455.41	22	455.403	1	455.403	1	493.4	7	493	60	233.527
Na	156	589.592	174	295	4940	330.237	30	589.592	415	589.592	13	588.995	22	589	200	589	2400	588.995
K	2160	766.491	493	383	1090	766.491	1400	766.49	310	766.491	189	766.491	300	766.5	300	766	4800	766.491

[a] ug/L

[b] nm; Non-recommended wavelengths are underlined.

TABLE 5B. PARTICIPATING LABORATORIES LIMIT OF DETECTION (LOD) AND LIMIT OF QUANTITATION (LOQ) FOR EACH ELEMENT*

	LABORATORY																	
	A		B		C		D		E		F		G		H		I	
ELEMENT	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ	LOD	LOQ
Al	5.9	19.6	4.4	14.7	9.2	30.6	1.1	3.5	9.6	32.0	1.6	5.3	0.9	2.8	5.0	16.7	8.0	26.6
Sb	2.3	7.5	1.8	5.9	4.2	14.0	3.5	11.7	5.8	19.3	4.7	15.5	1.3	4.2	5.0	16.7	3.0	10.0
As	6.8	22.5	2.9	9.7	5.6	18.5	20.0	66.6	4.6	15.3	10.0	33.3	1.1	3.7	1.5	5.0	10.0	33.3
Be	0.2	0.7	0.2	0.5	0.1	0.4	0.1	0.2	0.2	0.5	0.1	0.2	0.1	0.2	0.2	0.5	0.2	0.5
Cd	0.2	0.7	0.2	0.8	0.2	0.8	0.5	1.7	0.2	0.7	0.9	3.0	0.2	0.7	0.2	0.5	0.3	0.8
Ca	4.7	15.5	0.5	1.6	47.0	156	0.8	2.5	14.0	46.6	0.3	0.8	0.2	0.7	3.5	11.7	225	749
Cr	0.4	1.3	0.3	1.1	0.4	1.4	1.6	5.2	0.5	1.5	0.4	1.2	0.2	0.7	0.7	2.2	0.5	1.7
Co	0.8	2.7	0.3	1.1	1.2	3.8	0.6	2.0	1.5	5.0	0.6	1.8	0.2	0.7	0.2	0.7	1.9	6.3
Cu	0.8	2.7	0.3	1.0	1.2	4.0	0.5	1.7	0.5	1.7	0.2	0.5	0.2	0.5	0.7	2.2	0.9	2.8
Fe	0.5	1.7	0.3	1.1	3.7	12.2	0.5	1.7	3.0	10.0	0.4	1.3	0.2	0.5	1.0	3.3	4.0	13.3
Pb	0.5	1.7	2.7	8.9	3.4	11.2	3.6	11.8	6.2	20.6	3.1	10.3	1.8	5.8	10.0	33.3	9.0	30.0
Mg	11.9	39.6	0.4	1.3	36.0	120	0.1	0.3	15.5	51.6	1.3	4.2	0.1	0.2	1.0	3.3	180	599
Mn	0.2	0.5	0.2	0.5	0.6	2.0	0.1	0.3	0.2	0.7	0.1	0.2	0.1	0.2	0.1	0.3	0.6	1.8
Mo	1.5	5.0	0.5	1.7	0.8	2.5	3.0	10.0	0.9	2.8	0.8	2.7	0.2	0.7	0.3	1.0	1.5	5.0
Ni	1.0	3.3	0.5	1.7	1.4	4.5	0.9	2.8	1.2	3.8	1.0	3.3	0.4	1.3	1.0	3.3	1.6	5.2
Se	14.6	48.6	4.2	13.8	8.1	27.0	10.0	33.3	6.3	21.0	11.0	36.6	2.1	6.8	5.0	16.7	29.5	98.2
Ag	0.5	1.7	0.8	2.6	0.7	2.3	0.2	0.7	0.4	1.3	0.3	1.0	0.2	0.5	0.5	1.7	1.0	3.3
Tl	9.1	30.1	4.0	13.2	5.8	19.3	20.0	66.6	4.2	14.0	9.5	31.5	2.5	8.2	10.0	33.3	15.0	50.0
V	1.1	3.5	0.3	1.0	1.0	3.2	2.5	8.3	0.9	2.8	0.3	0.8	2.5	8.3	0.2	0.5	1.8	5.8
Zn	0.6	2.0	0.2	0.5	0.9	3.0	0.6	2.0	0.5	1.5	0.2	0.7	0.1	0.3	0.2	0.5	0.9	2.8
Ba	0.3	0.8	0.2	0.7	0.9	2.8	0.2	0.5	1.1	3.7	0.1	0.2	0.1	0.2	0.4	1.2	3.0	10.0
Na	7.8	26.0	8.7	29.0	247	822	1.5	5.0	20.8	69.1	0.7	2.2	1.1	3.7	10.0	33.3	120	400
K	108	360	24.7	82.1	54.5	181	70.0	233	15.5	51.6	9.5	31.5	15.0	50.0	15.0	50.0	240	800

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* The LOD and LOQ values were calculated from the IDL values in Table 5A, and they are given in mg/kg for comparison with solids data (adjusted for dilution factor of 50).

The ranges and arithmetic means of the reported IDL's, along with the "Estimated Instrumental Detection Limits," from Table 1 of Method 6010, are listed in Table 6 along with Method 6010 instrumental detection limits required by the present study. For comparison, the EPA CLP "Contract Required Detection Levels" (CRDL's) of each element are also given.

METHOD 6010 PERFORMANCE DATA

The analytical results for all the performance evaluation materials are presented in Tables 7 through 11. The analytical values resulting from the MSA are denoted with an asterisk. When analytical values were below the IDL determined by the participating laboratory, the laboratory IDL was to be reported in parenthesis with the alphabetic symbol "ND," as recommended (8) and as given in the following Tables. However, sometimes the laboratories reported "apparent detection limits" (IDL's or LOD's) that were different from their corresponding IDL's or LOD's (Table 5). These apparent detection limit values are given in parenthesis with "ND" and they are flagged by a double asterisk "**" in Tables 7, 9, and 10. The measurements that are between the IDL or LOD of the laboratory and the limit of quantitation (LOQ, 3.33 times the IDL) are indicated as detected by a "D" (7). The arithmetic means and percent RSDs are also given. The number of laboratories whose data was used in the calculations of the means and standard deviations are indicated by "n." When elemental concentrations were near the IDL's, the laboratories reported a measured value or "ND" depending on their IDL. In these cases, the values in parenthesis are either the detection limit (IDL or LOD) or an apparent detection limit reported by the laboratory (discussed above). All of these parenthetical values were excluded in the statistics. Caution must be exercised when considering the statistical data when three or more laboratories reported "ND" as indicated by a value for "n" of 6 or less. This situation is particularly noteworthy for the unspiked solids in Table 9, especially for the elements Sb, As, Mo, Se, Ag, and Tl.

Method 6010 Performance Evaluation Materials- The Spiked Bulk Digests

The results from the determination of 23 elements in the 7 spiked bulk digests are given in Table 7. Mean values and percent RSD's are also given in Table 7.

Method 6010 Blind QC Solutions

The analytical results for the Method 6010 QC solutions are found in Table 8. The mean values and percent RSDs are also given.

TABLE 6. INSTRUMENTAL DETECTION LIMIT SUMMARY (ug/L)

Element	Range for Participating Laboratories	Mean for Participating Laboratories	6010 Study Required IDL	CLP[#] CRDL	UNLV[+] Recommended Required IDL
Al	17-192	101	200	200	100
Sb	25-116	70	200	60	70
As	22-400	139	200	10	100
Be	1-4	2.4	5	5	2
Cd	3-18	6.4	20	5	5
Ca	4-4500	660	5000	5000	50
Cr	4-31	11	30	10	10
Co	4-38	16	50	50	20
Cu	3-24	11	30	25	15
Fe	3-80	30	100	100	30
Pb	10-200	89	200	5	70
Mg	1-3600	550	5000	5000	30
Mn	1-12	4.3	20	15	4
Mo	4-60	22	30	**	15
Ni	8-31	20	60	40	20
Se	41-590	200	300	5	150
Ag	3-20	10	30	10	10
Tl	49-400	180	200	10	150
V	3-50	23	50	50	20
Zn	2-18	9	20	20	10
Ba	1-60	13	200	200	15
Na	13-4940	930	5000	5000	150
K	189-4800	1230	5000	5000	500

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* Potassium determination is highly dependent upon operating conditions and plasma position so a value was not included.

** Molybdenum is not assayed in the CLP.

[#] CLP is Contract Laboratory Program of the EPA and CRDL is the Contract Required Detection Levels (where atomic absorption is necessary for some elements).

[+] UNLV is University of Nevada at Las Vegas.

METHOD 3050/6010 PERFORMANCE DATA

Method 3050/6010 Performance Evaluation Solids

The results from the analysis of the 7 solids are given in Tables 9 and 10. Table 9 presents the results for the duplicate unspiked solids and Table 10 presents the results for the duplicate spiked solids.

Method 3050/6010 Blind QC Solutions

The results from the analysis of the Method 3050/6010 QC solutions are presented in Table 11. The arithmetic mean values percent RSD's, the target concentrations, and the ratio of the mean to the target concentration of the elements in the QC solutions are given.

DATA REPORTING/AUDITS

The data packages from the participating laboratories (excluding the two referee laboratories) were all received after the required 30-day turnaround time, and lateness varied from 12 days to almost one month. The compliance audits revealed that the data package quality ranged from near perfect to highly deficient. The major deficiency was in regard to the application of the method of standard additions. At one extreme, one laboratory did not perform any MSA (this deficiency was eventually rectified), and the other extreme was that one laboratory applied the MSA to almost all analyses whether or not they were required by the criteria set forth in Method 6010. One laboratory also found a creative way of avoiding the application of the MSA through the extreme dilution of samples. The details on the results of the two data audits can be found in the corresponding audit reports, which are provided in Appendix G.

TABLE 7. METHOD 6010 SPIKED BULK DIGESTS DATA SUMMARY[a]

RIVER SEDIMENT

ELEMENTS	CONCENTRATION (ug/L) LABORATORY A	B	C	E	F	G	H	I	n[b]	MEAN	%RSD
Al	107000	143000	93500	94200	102000	96400	98400	144300	8	110000	19
Sb	13400	20400	15360	14200*	4690	5600	4240*	11640	8	11200	52
As	6960	7920	3455	5650*	6020	6780*	6280	6400	7	6570	11
Be	956	883	912	1020	866	991	988	940	8	945	5.8
Cd	1090	1040	1160	1400	1110	1190*	1060	977	7	1090	6.6
Ca	524000	566000	466700	567000	434000	552000	544000	499600	8	519000	9.4
Cr	542000	567000	517000	584000	494000	534000	526000	568000	8	541000	5.5
Co	1210	1530	1105	1370	1050	1100*	1160	1036	8	1190	14
Cu	2870	2770	2540	2620	3380	2790	2670	2635	7	2700	4.3
Fe	1930000	1810000	1526000	1920000	1690000	85200	1710000	1663000	7	1750000	8.3
Pb	16500	17500	3660	18700	17300	17800*	18200*	14920	7	17300	7.2
Mg	124000	129000	106000	132000	115000	128000	128000	110000	8	121000	8.1
Mn	9930	13700	12100	15300	13900	14300*	13500	11900	8	13100	13
Mo	1440	1570	(30)ND**	1360	1375	865	1220	470	7	1040	33
Ni	1700	2250	1490	1450	1790	1780*	1600*	(40)ND**	6	1640	8.9
Se	10200	8040	(300)ND**	7190*	5590	7530	7470	(9400)ND**	5	7160	13
Ag	971	883	486	759	1560	1100*	923	770	7	842	23
Tl	6700	4540*	5016	3990	5160	4260	4840*	3690	7	4500	13
V	1290	(5.8)ND	(50)ND**	1690	241	570	1280	(1500)ND**	5	1010	58
Zn	32400	29000	29100	34300	33600	22300*	30200	31770	7	31500	6.7
Ba	1990	1920	1705	1780	2170	1900	1904	1540	8	1860	10
Na	29400	60100	44800	55700	26700	27900	25100	28800	8	37300	38
K	20300	20400	18100	20300	20900	18300	17100*	18300	8	19200	7.4

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[a] Outlier data are underlined. ND indicates not detected (IDL is given in parentheses). Note that some laboratories reported an "apparent detection limit" in parenthesis that does not correspond to the value that they reported as the IDL (Table 5A). A "D" indicates a value between the IDL and LOQ (LOQ=3.33XIDL).

[b] The number of laboratories whose data was used in the calculations of the means and standard deviations, laboratory D did not submit ICP data.

*Determined by MSAs.

**The IDL value given in parentheses differs from the IDL reported by the corresponding laboratory (Table 5A.)

(continued)

TABLE 7. (continued)

FLY ASH

ELEMENTS	CONCENTRATION (ug/L) LABORATORY A	B	C	E	F	G	H	I	n	MEAN	%RSD
Al	341000	403000	260000	411000	303000	324000	298000	296700	8	330000	16
Sb	6530	27300	356*	5050*	658	3480*	4110	15520	6	3360	73
As	7500	37200	27800	53500*	3490	16100*	8000	14000	8	20900	83
Be	3160	2424	5040*	4240	7600	2320	703	6200	8	3960	57
Cd	969*	1300*	904	1070*	940	970*	956	527	6	968	5.7
Ca	87200	81000	82000	223000*	89700	65600*	92400	92000	6	87400	5.6
Cr	2200	3130*	(30)ND**	2900*	1600	1140*	1400	2179	7	2080	36
Co	1210	1560	1130*	1380*	1220	(3)ND**	1110	(760)ND**	6	1200	21
Cu	1950	1950	1520	1890	2040	1870	6560	1140	6	1870	9.7
Fe	661000	636000	551000	638000	525000	630000	632000	542600	8	602000	8.8
Pb	5000	11500*	3540	3860*	3820	6220*	5520*	4050	7	4570	22
Mg	16900	14700	16100*	11600	16100	12900*	18000	12600	8	14900	15
Mn	283	2130	1400*	1950*	1950	1900*	1990	1584	7	1840	14
Mo	1020000	1080000	847000	552000*	851000	1010000	986000	780800	8	891000	19
Ni	1560	615*	(60)ND**	1730*	1670	1550*	1510*	1366	6	1560	8.1
Se	8240	14100	(300)ND**	6050*	5850	3770	6090	5760	5	6400	16
Ag	1160	1630	(30)ND**	(8)ND	1540	(3)ND	231	(20)ND	3	1440	17
Tl	8150*	6350	629*	(420)ND*,**	7580	(49)ND	4800*	(19200)ND**	4	6720	22
V	996000	(5.8)ND	(50)ND**	1120000	1010000	(2)ND**	1010000	907000	5	1010000	7.5
Zn	2150	2170	1880	1460	2380	819*	2100	2230	6	2150	7.6
Ba	14500	15500	12700	12100	13500	12700	13100	12400	8	13300	8.7
Na	17100	38800	9250	27600	12700	14000	15600	25100	8	20000	49
K	49100	47200	42600	47100	47400	44800	47200	46200	8	46400	4.2

(continued)

TABLE 7. (continued)

ESTUARINE SEDIMENT

ELEMENTS	CONCENTRATION (ug/L) LABORATORY A	B	C	E	F	G	H	I	n	MEAN	%RSD
Al	360000	526000	87800	347000	358000	365000	357000	365700	6	359000	1.9
Sb	4710	5880	5140	4780	5290	5040	4440	4930	8	5030	8.7
As	5000	7660	4850	16500*	4330	4950	4800	6320	7	5420	22
Be	998	925	911	919	921	1040	950	945	8	951	4.8
Cd	950	892	780	1030*	913	927	899	900	8	911	7.6
Ca	78000	72000	74100	84200	71600	75200	78000	77700	8	76300	5.3
Cr	1600	1975*	1722*	1600	1840	1670	1630	1735	8	1720	7.6
Co	1120	1020	1040	1050	1200	1060	1160	984	8	1080	6.8
Cu	1210	1130	1055	1080	1440	1220	1180	639	6	1150	6.0
Fe	544000	534000	477000	511000	478000	531000	536000	447400	8	507000	6.0
Pb	4860	5270	5000	6890*	5360	4770	6020*	4930	6	5030	4.7
Mg	160000	158000	143000	171000	148000	161000	128000	137600	8	151000	9.4
Mn	4100	4630	5060	5480	5740	5240	5600	5107	8	5120	11
Mo	1170	1410	(30)ND**	1020	663	0.899	912	730	6	984	28
Ni	1400	1580	1385	1390*	1490	1330	1400*	1412	8	1420	5.4
Se	7880	10100	4310	7010	7460	8180	7230	8070	6	7640	6.2
Ag	906	814	511	251	1440	878	913	520	8	779	46
Tl	4580*	1690	4280	(84)ND*	5000	4530*	5360*	3870	7	4190	29
V	1830	1580	1620	1800	1880	1800	1720	1970	8	1770	7.3
Zn	3040	2080	2600	3280	3360	3310*	3220	2830	8	2960	15
BA	1760	1710	1640	1670	1900	1720	1590	1550	8	1690	6.4
NA	214000	204000	196000	215000	195000	193000	194000	212000	8	203000	4.7
K	85000	82300	76100	86100	82900	81300	20100	88500	7	83200	4.8

(continued)

TABLE 7. (continued)

MINE TAILING

ELEMENTS	CONCENTRATION (ug/L) LABORATORY A	B	C	E	F	G	H	I	n	MEAN	%RSD
Al	381000	540000	304000	333000	362000	345000	31000	351300	6	346000	7.6
Sb	4440	5890	4820	4540	5070	4870*	4810	4750	7	4760	4.4
As	16000	18800	17600	10100	18100	16800	17900	17000	7	17500	5.3
Be	875	839	920	990*	810	991	952	842	8	902	7.9
Cd	844	1060*	768	1040*	915	856*	924	800	8	901	12
Ca	226000	234000	190000	236000	196000	232000	198000	213600	8	216000	8.7
Cr	1060	2690*	2000	(9)ND	1890	1210	1260*	1049	7	1594	39
Co	987	910	900	1100*	1230	1120*	1060	835	8	1020	15
Cu	5770	4930	5530	6360*	7090	5940	5600	1229	7	5890	12
Fe	288000	240000	249000	249000	231000	267000	239200	222400	8	248000	8.4
Pb	124000	123000	6480	121000	116000	76200*	102000	106400	6	115000	8.0
Mg	329000	301000	258000	344000	286000	305000	299000	257600	8	297000	10
Mn	1870000	1820000	1742700	1850000	1667000	1740000	1670000	1611000	8	1750000	5.5
Mo	2020	2900	1400	2100	2430	2270*	2146	1690	8	2120	21
Ni	1280	1510	1260	1530*	1590	1340*	1080	1414	8	1380	12
Se	7960	10400	6030	7690	7950	8130	7610*	5530	8	7660	19
Ag	831	1030	896	404	1590	961	1010	690	7	832	27
Tl	10500*	1100	7380	(84)ND	6500	5580*	5410*	(19200)ND**	5	7070	29
V	1290	883	1090	1310	1460	1290*	1220	894	8	1180	18
Zn	8520	7200	7630	11410	10100	9510*	9080	7907	8	8920	16
Ba	9180	10600	8040	9280	10500	8800	9080	7890	8	9170	11
Na	76800	88000	80500	70600	70000	74300	72400	78800	8	76400	7.9
K	191000	189000	158500	183000	180000	167000	154000	180800	8	175000	7.9

(Continued)

TABLE 7. (continued)

HAZARDOUS WASTE 1

ELEMENTS	A	B	C	E	F	G	H	I	n	MEAN	%RSD
	CONCENTRATION (ug/L) LABORATORY										
Al	123000	155000	108000	125000	134800	124000	115000	135400	8	127000	11
Sb	4980	5160	5020	4790	5300	5020	4390	4780	8	4930	5.6
As	5410	5910	4010	4430	5370	4730*	4660	4670	8	4900	13
Be	933	868	928	1010	880	964	976	864	8	928	5.8
Cd	979*	785	844*	1040	992	997*	866	789	8	912	11
Ca	1440000	1490000	1290000	1490000	1220000	1460000	1450000	1203000	8	1380000	8.8
Cr	2760	2620	2880*	2970	3240	2970*	2940	2905	8	2910	6.2
Co	1040	872	1100*	1090	1240	1090*	1060	909	8	1050	11
Cu	4050	3800	3680	4020	4820	4050	3910	3659	7	3880	4.4
Fe	395000	353000	360000	357000	347000	372000	371000	312600	8	358000	6.6
Pb	8370	8550	7420	9810	10000	8150	10600*	6870	8	8720	15
Mg	518000	497000	438000	526000	488000	478000	486000	397600	8	479000	8.8
Mn	6880	6460	7690*	8610	8540	7710*	7760	6965	8	7580	10
Mo	1080	1270	92	1050	1300	1060*	1000	670	7	1060	20
Ni	1300	1360	1250	1330	1590	1370*	1500*	1202	8	1360	9.4
Se	8180	8570	5120	7800	7590	7810	6890	7120	7	7710	7.5
Ag	894	489	416	675	1560	875*	940*	650	8	812	44
Tl	5810*	3920*	4160	3890	5360	3800*	5100*	3530	8	4440	19
V	1280	975	1180	1410	1400	1190	1330	1176	8	1240	11.6
Zn	4200	4100	4800*	3970*	5000	4300*	4360	3874	8	4330	9.1
Ba	4680	4380	3650*	4110	5210	4430	4520	3880	8	4360	11
Na	14800	19100	11600	19900	16000	14600	16400*	13800	8	15800	17
K	25700	26800	22600	25600	28300	23800	29300*	24400	8	25800	8.8

(continued)

TABLE 7. (continued)

INDUSTRIAL SLUDGE

ELEMENTS	CONCENTRATION (ug/L) LABORATORY A	B	C	E	F	G	H	I	n	MEAN	%RSD
Al	238000	308000	232000	23300	258000	245000	224000	272400	7	254000	11
Sb	4540	5550	4990	4580	4810	4650	4700	4720	7	4710	3.2
As	5040	7020	4610	4750	3640	3040*	4660	5710	8	4810	25
Be	901	878	890	1000	842	975	862	856	8	901	6.4
Cd	1190	1190	497*	1760	1250	1240	1210	1288	6	1230	3.1
Ca	1230000	1380000	1240000	1310000	1040000	1310000	1310000	1172000	8	1250000	8.5
Cr	1780	1790	1846	1690	2000	1780	1880	1987	8	1840	5.8
Co	1020	1150	1116	1020	1120	1020	1120	950	8	1060	6.7
Cu	5940	5110	5690	7160	7030	6130	5980	5649	8	6090	11
Fe	318000	323000	271800	302000	282000	314000	316000	276600	8	300000	6.9
Pb	285000	303000	244000	290000	285000	286000	267000	277000	7	285000	3.9
Mg	38900	37900	36000	45400	43800	24600*	40100	39600	7	40400	8.0
Mn	14900	14400	13200	15600	15100	11400*	3570	13400	7	14000	11
Mo	1060	1170	190	944	1050	867	854	720	7	952	16
Ni	3590	3880	3710	4120	4140	2920*	3900	3929	7	3900	5.1
Se	7640	9310	5850	7240	7150	7820	7520	7510	8	7500	13
Ag	949	404	343	854	1590	904	843	660	8	818	47
Tl	6920*	4470*	5248	3720	5570	2460*	4070	3760	8	4530	30
V	1050	1010*	1010	1080	1180	1080	1140	1079	8	1080	5.5
Zn	27600	25400	23800	32400	29900	10000*	27000	29660	7	28000	10
Ba	175000	187000	151000	165000	169000	169000	156000	147000	8	165000	8.0
Na	44100	44600	59300	47300	50700	43900	10700	44700	6	45900	5.8
K	17200	19000	15800	18100	21300	17300	13600	17000	8	17400	13

(continued)

TABLE 7. (concluded)

ELECTROPLATING SLUDGE

ELEMENTS	CONCENTRATION (ug/L) LABORATORY A	B	C	E	F	G	H	I	n	MEAN	%RSD
Al	124000	158000	113000	110000	143000	124000	111000	135800	8	127000	13
Sb	6260	9960	7030	2960*	5430	5210	4790	5290	7	5280	24
As	5260*	6800	4350	5190	4880	5720	5450	5410	7	5180	8.6
Be	839	1090*	902	1020	887	982	856	563	7	939	9.9
Cd	2520	3300*	2520	1060000	2965	2940	2790	3008	7	2860	9.8
Ca	979000	1010000	942000	3240	864000	1030000	989000	865200	7	954000	7.0
Cr	154000	154000	140000	941	153000	152000	148000	179000	7	154000	7.8
Co	917	1040	916	151000	1130	1070*	1140*	864	7	1010	11
Cu	16100	15400	15300	16700	17700	15100	14000	14340	8	15600	7.8
Fe	678000	550000	554000	939000	589800	642000	642000	567400	7	603000	8.4
Pb	25800	24100	20070	25300	27500	23600	26200*	23900	7	25200	5.6
Mg	33000	33400	30290	43000	39300	21700*	42200	35300	8	34800	20
Mn	3750	5740*	5190	6240	6710	5720	6400	5323	7	5900	9.6
Mo	1320	1890	(30)ND**	2100	1450	1070	1050	700	7	1370	36
Ni	8500	9100	2350	10100	10470	10500*	8480	9324	7	9500	9.6
Se	10600*	9510	3725	7690	8240	9090	8000	7690	7	8690	13
Ag	812	784	565	651	1800	908	917	620	7	751	19
Tl	6640*	4080*	4600	(84)ND	5330	4840*	5840	3850	7	5030	20
V	1170	448	659	1260	1490	1110	1170	1250	6	1240	11
Zn	262000	264000	221600	269000	273000	266000	254000	273200	7	266000	2.5
Ba	1660	1730	1520	1600	2220	1710	1720	1530	8	1640	20
Na	1490000	1440000	1583000	1300000	1141000	1370000	1300000	1408000	8	1380000	9.8
K	49100	54300	46300	51900	51200	53000	47600	53800	8	50900	5.8

TABLE 8. METHOD 6010 QC SOLUTIONS DATA SUMMARY[a]

ELEMENT	CONCENTRATIONS (ug/L) LABORATORY A	B	C	E	F	G	H	I	TARGET	n[b]	MEAN	% RSD	MEAN/ TARGET
Al	13500	15300	14700	16700	13800	14800	14300	15000	14800	8	14800	6.3	1.00
Sb	13100	15100	16200	14100	15000	16200	16500	14700	14800	8	15100	7.7	1.02
As	13700	18400	15500	14500	15000	15400	15400	13100	14800	7	14700	6.4	0.99
Be	3530	3610	3860	3640	4030	4140	3760	3630	3700	8	3780	5.8	1.02
Cd	3380	3220	3480	3740	3480	3970	3770	3808	3700	8	3610	7.0	0.97
Ca	13600	14800	14600	15800	13200	16200	15600	15900	14800	8	15000	7.4	1.01
Cr	3300	3520	3855	3560	3830	3910	3680	4311	3700	8	3750	8.2	1.01
Co	3320	3220	3490	3490	3510	3890	3700	3554	3700	8	3520	5.9	0.95
Cu	3410	3280	3660	3720	3410	3690	3600	3884	3700	8	3580	5.6	0.97
Fe	13600	14200	13700	15200	14900	15600	15100	16000	14800	8	14800	5.9	1.00
Pb	13100	14600	6610	15000	14200	15800	14200	14000	14800	7	14400	5.9	0.97
Mg	13100	13300	13500	15500	13600	14900	15100	14100	14800	8	14100	6.5	0.96
Mn	3880	3380	3770	3800	3710	3890	3790	3760	3700	8	3700	4.3	1.00
Mo	3410	4170	3660	3600	3800	3870	3660	3390	3700	8	3700	6.9	1.00
Ni	3300	3810	3890	3680	3560	3860	3810	4450	3700	7	3700	5.7	1.00
Se	13500	17200	15500	14500	15800	16400	14800	14900	14800	8	15300	7.5	1.04
Ag	274*	3780	1150	3770	3720	3840	4010	3040	3700	8	3690	9.1	1.00
Tl	16900	16100	15600	14100	14300	16400	14200	13400	14800	7	15100	8.5	1.02
V	3250	3220	3390	3390	3660	3750	3570	3840	3700	8	3510	6.6	0.95
Zn	3320	3100	3390	3750	3500	4020	3680	3771	3700	8	3570	8.3	0.96
Ba	3520	3880	3595	3700	4240	3680	3610	3670	3700	7	3660	3.1	0.99
Na	13600	13800	13500	14700	15000	13700	13400	14200	14800	8	14000	4.2	0.95
K	13500	14600	13800	15500	15000	12700*	13300	14200	14800	8	14100	6.6	0.95

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[a] MSA data are marked with an asterisk, and outlier data are underlined.

[b] The number of laboratories whose data was used in the calculations of the means and standard deviations, laboratory D did not submit ICP data.

TABLE 9. METHOD 3050/6010 UNSPIKED SOLIDS DATA SUMMARY[a]

RIVER SEDIMENT

ELEMENT	CONCENTRATION (mg/kg) LABORATORY A	B	C	D	E	F	G	H	I	n[b]	MEAN	%RSD
Al	4520	6240	3920	3510	6870	3857	3980	5180	8950	9	5230	35
Sb	452	662	525	254	(5.9)ND	55*	0.51*	47	388	8	350	68
As	118	129	(10)ND**	47D	(4.7)ND	50*	86.3*	59	(163)ND**	6	82	44
Be	0.4*	0.20	0.76	0.495	(0.15)ND	0.65*	0.5	0.7	(0.15)ND	7	0.5	36
Cd	13	30*	12	12.4	13.8	9.27*	8.59*	6.9	9.8	9	11	21
Ca	30000	27600	28400	28100	31800	22885	28500	27000	31700	9	28400	9.5
Cr	30300	28500	32200	26800	38900	28200	27400	27900	35200	9	30600	13
Co	17	49*	17	49	17.9*	12.9*	4.6*	6.7	15	9	21	74
Cu	99	91	83	82.2	83.2	99.25	90	105	91	9	91	8.9
Fe	87500	96200	70000	67800	116000	51850	71200	82800	102000	9	82800	24
Pb	685	549	630	559	641	531.6*	673*	671	710	9	628	10
Mg	6680	6290	5700	6880	5800	5789	6710	7200	7500	9	6510	10
Mn	696	542	550	520	662	613	497*	660	750	9	611	14
Mo	27	38	(1.5)ND**	12.4	18*	10.2*	14.2	15	(1.5)ND	7	19	51
Ni	37	$\underline{74}$	30	20.2	19*	31.65*	30.6*	30	(63)ND**	7	29	18
Se	50	109	(15)ND**	(10)ND	(6.4)ND	14.25D*	40	75	(30)ND	5	58	62
Ag	1.7	2.6D	(1.5)ND**	2.48	(0.41)ND	0.75D*	0.9	(0.5)ND*	(1.0)ND	5	1.6	48
Tl	$\underline{53}$	(4.0)ND	13D	(20)ND	(4.3)ND	210*	(2.4)ND	(10)ND	(15)ND	2	17	33
V	17	(5.8)ND**	2.5D	19.3	43.8*	9.3*	(0.1)ND**	16	(36)ND**	6	18	78
Zn	1780	1990*	1500	1410	1560	1611	$\underline{978}$*	1600	1800	8	1660	11
Ba	51	47	45	43.6	52.4	50.88	44.3	52	36	9	47	11
Na	994	2640	2270	970	2830	898.7	850	1030	1060	9	1500	53
K	297D	443	311	367	688	320.3	420*	645	582	9	453	33

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[a] Outlier data are underlined. ND indicates not detected (LOD is given in parentheses). Note that some laboratories reported an "apparent detection limit" in parentheses that does not correspond to the value that they reported as the IDL (Table 5). A "D" indicates a value between the LOD and LOQ (LOQ=3.33 x LOD).

[b] The number of laboratories whose data was used in the calculations of the means and standard deviations.

*Determined by MSAs.

**The LOD value given in parentheses differs from the LOD reported by the corresponding laboratory (Table 5).

(continued)

TABLE 9. (continued)

RIVER SEDIMENT DUPLICATE

ELEMENT	CONCENTRATION (mg/kg) LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	3930	2960	4430	3870	6870	4816	4560*	5040	7530	9	4890	30
Sb	452	401	515	254	(5.9)ND	55*	1.4*	48	456	8	243	89
As	113	85	(10)ND**	45.10	(4.7)ND	50*	166	62	(163)ND**	6	87	53
Be	0.4*	(0.2)ND	0.81	0.495	(0.15)ND	0.7*	0.6*	0.7	(0.15)ND	6	0.7	18
Cd	12	10	12	11.4	9.41	9.27*	10.6*	8	9.5	9	10	13
Ca	29800	15400	24800	28100	21600*	23090	28500	27800	31100	9	25600	19
Cr	30000	17100	31100	26600	42800*	27500	27400	28100	37500	9	29800	24
Co	7.4*	17	16	47	15.6	12.85*	3	7.1	18	8	12	47
Cu	96	54	85	80.7	80.9	102.6	93	104	95	8	92	9.9
Fe	70800	53700	75900	62220	116000	81000*	76800*	80500	100000	9	79700	24
Pb	689	327	568	559	611	740*	840*	680	700	8	673	14
Mg	6530	3770	5920	6830	5090*	5679	6730*	7170	6790	8	6340	11
Mn	604	398	607	495	651	696	815*	664	756	9	632	20
Mo	27	22	(1.5)ND**	12.4	19.7*	27.65*	14.8*	13	(1.5)ND**	7	20	33
Ni	35	44	36	27.2	16	46*	50.7*	31	(63)ND**	8	36	32
Se	440	62	(15)ND**	(10)ND	(6.4)ND	96.5*	6.92*	77	(30)ND	5	57	60
Ag	1.7	(0.8)ND	(1.5)ND**	2.48	(0.41)ND	2.1*	1.2*	0.8*	(1)ND	5	1.6	38
Tl	46	(4.0)ND	140	(20)ND	(4.3)ND	20.70*	(2.4)ND	(10)ND	(15)ND	2	17	27
V	15	(5.8)ND**	(2.5)ND	17.8	29.2	1	(0.1)ND**	14	(36)ND**	6	15	66
Zn	1780	840	1420	1430	1550	1601	1410*	1650	1920	8	1590	12
Ba	50	28	48	42.6	50.3	52.25	50	53	38	8	48	11
Na	989	1520	2230	941	2760	859.6	890*	1080	1090	9	1370	50
K	237	272	404	339	713	476.4	532*	608	5260	9	456	35

(continued)

TABLE 9. (continued)

FLY ASH

ELEMENT	CONCENTRATION (mg/kg) LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	13700	15700	12200	12400	18800	16262	13200	16300	19800	9	15400	18
Sb	(10)ND**	44	(10)ND**	(3.5)ND	(5.8)ND	(3.7)ND*	(1.28)ND	6.40	(3)ND	1	6.4	--
As	131	196	113	103	94	113*	124	131	210	9	135	30
Be	2.1	1.5	2.4*	1.99	3.6	3.85*	2.95	4.1	3.1	9	2.8	32
Cd	1.8*	3	(1)ND**	0.9950	4	(0.65)ND*	0.93*	(0.15)ND	3.3	6	2.3	55
Ca	4300	3950	4670	4250	4810	4986	4420	5400	5360	9	4680	11
Cr	12	31	22	18.4	31.2	32.2	18.8	24	23	9	24	29
Co	6.2	10	90	9.45	14.1	14*	7.37*	11	12	9	10	27
Cu	24	25	27	26.4	29.8	39.2	28.6	35	35	9	30	18
Fe	25600	14300	11200	11700	39000	26800	9900	15500	21600	9	19500	49
Pb	(10)ND**	36	300	20.4	27.4*	30.9*	20.6	210	(36)ND**	7	27	23
Mg	610	626	721	672	875	948.1	465*	1030	880	9	759	24
Mn	(1)ND**	36	41	35.3	56.5	60.25*	38.1	48	46	8	45	30
Mo	27	31	(1.5)ND**	22.9	24.6	32.3*	24.4	23	19	8	26	17
Ni	16	29	220	16.9	29.2	40*	7.54*	25	29	9	24	40
Se	(15)ND	52	(15)ND**	(10)ND	(6.4)ND	(10)ND*	440*	(5)ND	(30)ND	0	--	--
Ag	(1)ND**	(0.8)ND	(1.5)ND**	0.995	(0.4)ND	0.50	(0.15)ND	(0.5)ND	(1)ND	2	0.8	47
Tl	(10)ND	(4.0)ND	(10)ND**	(20)ND	(4.2)ND	(6.5)ND*	2.6*	(10)ND	(15)ND	1	2.6	--
V	64	57	71	67.2	93.5	88.95	69.5	82	83	9	75	16
Zn	47	43	44	47.3	55.8*	65.8	35*	62	58	9	51	20
Ba	686	652	672	582	670	675.4	635	672	688	8	669	2.5
Na	2460	466	(2510)ND**	261	915	252.2	211	308	2800	6	289	29
K	1330	1440	1510	1470	2350	1851	1490*	2290	2090	9	1780	23

(continued)

TABLE 9. (continued)

FLY ASH DUPLICATE

ELEMENT	CONCENTRATION (mg/kg) LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	10500	17400	12200	11600	17800	15932	12600	15300	17600	9	14500	20
Sb	(10)ND**	96	(10)ND**	(3.5)ND	(5.8)ND	(2.15)ND*	(1.2)ND	(5)ND	(3)ND	0	--	--
As	139	214	119	107	84.5	118*	104*	127	216	9	137	35
Be	(2)ND*,**	2.3	2.9	1.99	3.55	3.75*	2.8*	3.9	3.2	8	3.1	22
Cd	3*	3	(1)ND**	0.995D	3.8	(0.65)ND*	0.5*	(0.15)ND	3	6	2.2	60
Ca	4520	4250	4630	4120	4900	4784	4280	5250	5140	9	4650	8.6
Cr	21	37	20*	18.4	29.1	31.05*	18	22	26	9	25	27
Co	12	12	8.2	13.9	13.2	13.7*	7.4*	10	13	9	12	20
Cu	31	28	27	25.9	29.8	38.95	28	34	33	9	31	13
Fe	7930	17800	9630	9900	34600	25293	9450	13400	21800	9	16600	55
Pb	20	48	30	19.4	47.4	28.45*	19.4*	200	(36)ND**	8	29	42
Mg	735	716	725	657	890	928.6	597*	971	850	9	586	16
Mn	(1)ND	42	39	34.8	54.5	58.85*	36.8	46	48	8	45	19
Mo	35	30	(1.5)ND**	23.4	22.9	29.45*	23.8	23	17	8	25	22
Ni	28	40	22	17.4	27.5	36.7*	19.3*	24	30	9	27	28
Se	(15)ND	61	(15)ND**	(10)ND	(6.4)ND	(10)ND*	23.6*	(5)ND	(30)ND	1	24	--
Ag	(1)ND**	(0.8)ND	(1.5)ND**	0.995	(0.4)ND	0.5D	(0.15)ND*	(0.5)ND	(1)ND	2	0.8	47
Tl	(10)ND	(4)ND	(10)ND**	(20)ND	(4.2)ND	(6.5)ND*	8.2*	(10)ND	(15)ND	1	8.2	--
V	76	62	68	65.7	92	87.35	67.5*	80	86	9	76	14
Zn	64	50	45	47.3	71.5	62.85	35.6*	59	56	9	55	20
Ba	656	653	620	582	690	710.8	625	671	678	9	654	6.1
Na	230	571	(2510)ND**	272	825	266.3	222*	295	2800	6	305	39
K	1660	1700	1570	1490	2300	1989	2400*	2190	2150	9	1940	18

(continued)

TABLE 9. (continued)

ESTUARINE SEDIMENT

ELEMENT	CONCENTRATION (mg/kg) LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	11830	17800	11500	13400	19600	15920	14400	17800	20400	9	15800	21
Sb	(10)ND**	55	(10)ND**	4.420	(5.9)ND	(3.04)ND*	(1.2)ND	(5)ND	(3.1)ND	1	4.4	--
As	130	83	(10)ND**	(20)ND	(4.7)ND	12.850*	13.1*	(1.5)ND	(163)ND**	3	13	1.0
Be	0.3*	3	0.9	0.49	0.662*	0.95*	0.85	1.2	0.56	8	0.7	37
Cd	2.6	4.4	(1)ND**	2.46	3.46*	1.250*	0.06*	(0.2)ND*	3.9	7	2.7	58
Ca	3640	3110	3520	3240	4110	3511	3160*	4008	4180	9	3610	11
Cr	27	44	37*	30.9	37.6	38.8	28.1*	38	55	9	37	22
Co	8.4	9.6	7.9	17.7	7.74	9.75*	6.65	8.4	8.2	8	8.3	12
Cu	14	12	10	13.8	8.75	16.4	12.8	14	14	9	13	18
Fe	25300	22700	22600	23700	27300	23793	24600	27200	29000	9	25100	8.9
Pb	20	43	29	22.1	35.4*	25.1*	18.4	200	64	8	27	33
Mg	8060	7120	7340	7370	8140	7415	7800	9180	9080	9	7940	9.5
Mn	168	181	199	198	237	234.1	202*	236	217	9	206	11
Mo	8.5	9.6	(1.5)ND**	(3)ND	(0.86)ND	(0.035)ND	2.4	(0.3)ND*	(1.5)ND	3	6.8	57
Ni	22	32	21	18.2	15.7	27.1*	20.6	23*	20	9	22	22
Se	(15)ND	63	(15)ND**	(10)ND	(6.4)ND	120*	23	160	(30)ND	3	17	33
Ag	(1)ND**	(0.8)ND	(1.5)ND**	0.98	(0.41)ND	1*	(0.15)ND	(0.5)ND	(1)ND	2	1.0	1.4
Tl	(10)ND	(4.0)ND	(10)ND**	(20)ND	(4.3)ND	40*	(2.4)ND	(10)ND	(15)ND	0	--	--
V	37	27	33	36.4	46.4	43.45*	38	44	47	9	39	17
Zn	116	84	91	99.7	104	102.1	105*	107	94	9	100	10
Ba	30	31	28	30	38.2	39.1	30.4*	36	36	9	33	13
Na	10800	8650	9380	10000	9820	8890	8450	10800	10300	9	9680	9.2
K	3170	2950	2900	3090	3970	3340	2760*	3860*	4030	9	3340	15

(continued)

TABLE 9. (continued)

ESTUARINE SEDIMENT DUPLICATE

ELEMENT	CONCENTRATION (mg/kg) LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	9220	20200	11300	13100	18400	15090	13800	17000	19900	9	15300	25
Sb	(10)ND**	55	(10)ND**	6.88D	(5.9)ND	(3.04)ND*	(1.2)ND	(5)ND	(3.1)ND	1	6.9	--
As	(10)ND**	93	(10)ND**	(20)ND	(4.7)ND	12.6D*	21.3*	(1.5)ND	(163)ND**	2	17	36
Be	0.2*	0.8	0.75	0.49	0.86	0.8*	0.8	1.1	0.61	9	0.7	34
Cd	2.3	3.5	(1)ND**	2.95	3	1.75D*	0.34	(0.2)ND*	3.3	7	2.4	45
Ca	3120	3170	3480	3130	4130	3617	3430	4010	4010	9	3570	11
Cr	21	36	38*	31.4	36.4	38.5	31.4	37	50	9	35	22
Co	7.5	9.5	7.9	18.7	7.53	10.1*	7.25*	8.4	8.1	8	8.3	12
Cu	13	11	9.5	14.3	9.36	15	12.6	14	14	9	12	17
Fe	21000	22300	22700	23200	26400	23860	24400	26800	29400	9	24500	11
Pb	22	40	35	29.5	47.8	23.2*	18.4	23	57	9	33	40
Mg	6680	6990	7350	7270	8040*	7285	7700	9080	8160	9	7620	9.5
Mn	192	182	213	196	233	233	199	238	209	9	208	8.5
Mo	9*	10	(1.5)ND**	(3)ND	(0.86)ND	(0.3)ND	2.2	(0.3)ND*	(1.5)ND	3	7.1	60
Ni	19	29	21	18.2	16.4	26.7*	20	23*	19	9	21	20
Se	(15)ND	63	(15)ND**	(10)ND	(6.4)ND	12D*	21.5*	18	(30)ND	3	17	28
Ag	(1)ND**	(0.8)ND	(1.5)ND**	.98	(0.41)ND	1*	(0.15)ND	(0.5)ND	(1)ND	2	1.0	1.4
Tl	(10)ND	(4.0)ND	(10)ND**	(20)ND	(4.3)ND	40*	(2.4)ND	(10)ND	(15)ND	0	--	--
V	32	27	34	35.9	46.7	43.45*	36.8	43	44	9	38	17
Zn	101	84	90	100	102	100.9	94.8*	107	95	9	97	7.2
Ba	27	29	30	44.2	38.6	36.2	29.4	34	33	9	33	16
Na	9710	8490	9630	9920	9970	9285	8300	11000	10500	9	9650	9.0
K	2600	3090	2770	3030	3940	3205	2720*	4450*	4060	9	3320	20

(continued)

TABLE 9. (continued)

MINE TAILING

ELEMENT	CONCENTRATION (mg/kg) LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	12800	16900	13200	12700	15100	12240	13400	14900	23700	8	13900	11
Sb	15	61	(10)ND**	4.21D	(5.8)ND	(2.4)ND*	(1.2)ND	(5)ND	(3.1)ND	2	27	110
As	850	527	711	510	315	603.5	570	704	773	9	618	26
Be	0.4D*	(0.2)ND	0.81	0.468	0.405D*	0.1D	0.7	0.7	0.57	8	0.5	46
Cd	2.6*	3.2	(1)ND**	0.935D	0.615D*	2.5D*	(0.2)ND	(0.2)ND	(4.1)ND**	5	2.0	56
Ca	9850	9360	9950	9860	10500	9150	8650*	10300	11000	9	9850	7.3
Cr	11	87	41	7.01	(0.46)ND	10	9.55	11	4.8	6	14	92
Co	8.4	8.6	6	11.2	6.31	8.3*	6*	6.9	3.7	9	7.2	29
Cu	264	192	229	197	245	250.5	230	267	61	8	215	30
Fe	10900	10500	9520	8560	12500	8200	9690	10300	12800	9	10300	15
Pb	6100	5290	5710	5844	6000	6951	3330*	5080	6640	8	5660	19
Mg	14800	12900	14100	13700	14800	12824	13600	16000	14900	9	14200	7.4
Mn	102000	86100	102000	82200	126000*	91900	84100	88100	106000	8	92800	10
Mo	72	74	32	44.4	59	77.5*	41.6*	55	46	9	56	29
Ni	22	37	21	13.6	22*	21.8*	4.2*	18	27	9	21	43
Se	71	129	(15)ND**	(10)ND**	(6.4)ND	(4.1)ND*	28.8*	(5)ND	(122)ND**	3	76	66
Ag	16	13	15	15.4	(0.41)ND	0.5D*	4.3*	(0.5)ND	7.6	7	10	60
Tl	261	(4.1)ND	98	(20)ND	(4.3)ND	100D*	3.1D*	(10)ND	(247)ND**	4	93	130
V	23	4.9	9.7	15	22	14.7	10.7*	18	(1.8)ND	8	50	42
Zn	412	320	395	324	347*	455.5*	218*	419	365	9	362	20
Ba	450	434	384	318	412	408.8	358	436	371	9	397	11
Na	3620	3640	3660	3070	3160	2926	2890	3780	3790	9	3390	11
K	7350	7480	7090	6500	14700	6330	6400	8320	8970	8	8130	32

(continued)

TABLE 9. (continued)

MINE TAILING DUPLICATE

ELEMENT	CONCENTRATION (mg/kg) LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	9380	16700	12500	12300	15800	12015	14200	16600	19800	9	14400	22
Sb	14	60	(10)ND**	(3.5)ND	(5.8)ND	(2.9)ND*	(1.2)ND**	(5)ND	(3.1)ND	1	14	--
As	836	497	728	496	292	598	882*	695	699	9	636	29
Be	0.40*	0.60	0.81	0.468	0.503*	0.10	0.7	0.6	0.46	9	0.5	37
Cd	1.3*	3.4	(1)ND**	0.9350	0.82*	2.40*	(0.2)ND	(0.2)ND	(4.1)ND**	5	1.8	61
Ca	9590	8980	9290	9910	10500	8585	8460*	10300	11400	9	9670	10
Cr	8.8	43	38*	6.55	(0.46)ND	10*	10.3	10	6.3	8	17	89
Co	8	8.6	5.7	10.8	12.2*	8*	6.1*	6.7	3.9	9	7.8	31
Cu	260	203	230	195	244	241	242	266	34	8	235	11
Fe	7190	9630	8790	8140	13200	8045	10200	10400	12700	9	9810	21
Pb	6220	5230	6280	5700	5380	5921	3540*	5510	6190	9	5550	15
Mg	13200	13000	13700	13500	15100	12372	14500	16900	16300	9	14300	11
Mn	105000	84400	101000	83500	75900	90560	88900	91300	110000	9	92300	12
Mo	70	69	31	43	61	70*	45.5*	54	47	9	55	24
Ni	20	29	28*	14	27.2*	22.6*	4.7*	18	23	9	21	37
Se	65	125	(15)ND**	(10)ND	(6.4)ND	(9.3)ND*	22.8*	15	(122)ND**	4	57	88
Ag	16	10	13	15.4	(0.4)ND	0.50*	5.04*	(0.5)ND	7	7	9.5	60
Tl	258	(4.1)ND	99	(20)ND	(4.3)ND	110*	14.7*	(10)ND	(247)ND**	4	96	120
V	19	3.4	8.7	14	28*	14.2	11.3*	18	(1.8)ND	8	15	51
Zn	388	305	387	321	304	482*	249*	418	368	9	358	20
Ba	449	403	388	317	433	437	375	432	397	8	414	6.5
Na	3650	3570	3370	3030	3250	2433	2980	3900	3890	9	3340	14
K	6680	7120	6990	6360	7880	6315	6600	8850	9400	9	7350	15

(continued)

TABLE 9. (continued)

HAZARDOUS WASTE #1

ELEMENT	CONCENTRATION (mg/kg) LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	5130	6860	5000	4940	7330	5545	6250	6140	8870	9	6230	21
Sb	16	30	(10)ND**	8.480	(5.9)ND	8.50*	(1.2)ND	(5)ND	(3.0)ND	3	11	39
As	35	39	(10)ND**	(20)ND	(4.7)ND	31.90*	15*	8.4	(40)ND**	5	26	52
Be	0.30*	0.8	0.80	0.499	0.662*	0.7	0.8	1.1*	0.66	9	0.7	30
Cd	3.7	4.1	2.3	2.99	3.61	2.10	1.8	1.7	3.4	9	2.9	31
Ca	80200	71500	73900	70400	81900	59200	75100	73100	79900	8	73900	9.3
Cr	103	89	101*	81.3	95.7	120	112*	101	100	9	100	11
Co	8.2	8.5	7.1	5.49	12.2	10.6*	8.35*	8.2*	7.2	9	8.4	25
Cu	158	126	150	115	150	150	150	169	136	9	145	12
Fe	20300	18000	15300	15300	22500	15440	18200	17600	22400	9	18300	16
Pb	203	167	184	218	189	199	208*	213*	184	9	196	8.4
Mg	28100	24800	25200	34700	28800	23355	25200	25100	28900	9	26000	7.9
Mn	334	292	330	278	361	350	379*	351	322	9	333	9.7
Mo	11*	9.6	(1.5)ND**	(3)ND	7.18	7.4*	5.45	5.1	(1.5)ND	6	7.6	30
Ni	20	26	17	12.5	16.5	19.4	21*	19*	19	9	19	19
Se	320	35	(15)ND**	(10)ND	(6.4)ND	150*	(2.0)ND	140	(30)ND	4	24	46
Ag	1.50	(0.8)ND	(1.5)ND**	2.49	(0.41)ND	2.7*	1.1	1.10	(1.0)ND	5	1.7	41
Tl	34	(4.0)ND	(10)ND**	(20)ND	(4.3)ND	20.70*	(2.4)ND	(10)ND	(15)ND	2	27	34
V	13*	10	18	14.0	21.9	17.7*	19*	21	21	9	17	24
Zn	186	132	146	141	183	206*	187*	171	155	9	168	15
Ba	190	169	166	128	174	187	172	158	156	8	172	7.2
Na	200	569	(251)ND	218	606	224.8	210	242	2370	8	313	84
K	530	756	532	539	897	643	635	1040	970	9	727	27

(continued)

TABLE 9. (continued)

HAZARDOUS WASTE DUPLICATE #1

ELEMENT	CONCENTRATION (mg/kg) LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	4900	7950	5220	5340	5550	5635*	5850	6700	7160	9	6030	17
Sb	14	29	(10)ND**	(3.5)ND	(5.9)ND	20*	(1.2)ND*	(5)ND	(3)ND	3	21	36
As	26	38	(10)ND**	(20)ND	(4.7)ND*	37.7*	12.3	9.3*	(40)ND**	5	25	55
Be	0.4	1.1	0.75	0.499	0.611*	0.7	0.8	1.1*	0.61	9	0.7	31
Cd	3.2	3.8	2.7	2.49	3.36	1.80	6.05	1.9	3.2	9	3.1	42
Ca	78500	72100	74300	72400	64600	59700*	73800*	72600	79400	9	71900	8.7
Cr	101	89	102	85.8	80.4	116*	102*	101	102	9	89	11
Co	7.2	7.9	7	5.49	8.04*	11	6.05	8.3*	6.8	8	7.5	22
Cu	154	126	138	133	124	155	148	148	143	9	141	8.2
Fe	17400	17300	15500	16200	19500	15525	17300*	18400*	20400	9	17500	9.7
Pb	204	181	191	178	180	201	191*	210	166	9	189	7.5
Mg	27500	24700	25400	25900	27000	23570	24500*	25600	25800	9	25600	4.8
Mn	329	287	335	300	310	356	357	344	314	9	326	7.6
Mo	11	9.8	(1.5)ND**	(3)ND	6.77*	8.1*	5.1*	5.6*	(1.5)ND	6	7.7	30
Ni	18	24	17	15.5	15.2*	18.1*	18.5*	19*	16	8	17	9.0
Se	260	33	(15)ND**	(10)ND	(6.4)ND	160*	(2.0)ND	150	(30)ND	4	22	38
Ag	0.70	(0.8)ND	(1.5)ND**	2.49	(0.41)ND	1.6*	1.8	0.90	(1.0)ND	5	1.4	41
Tl	240	(4.0)ND	(10)ND**	(20)ND	(4.3)ND	36*	(2.4)ND	(10)ND	(15)ND	2	30	28
V	17	10	15	16.5	18.7	17.1*	16*	21	19	8	17	19
Zn	183	134	143	147	156	198	181	167	154	9	163	13
Ba	180	159	161	143	149	177	158	158	169	9	162	7.5
Na	196	572	(251)ND	254	529	249	201	251	217	8	309	49
K	496	756	566	584	740	611	671	1110	870	8	662	18

(continued)

TABLE 9. (continued)

INDUSTRIAL SLUDGE

ELEMENT	CONCENTRATION (mg/kg) LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	13600	12900	11700	12000	16300	12254	14000	14600	17500	9	13900	14
Sb	14*	44	(10)ND**	(3.5)ND	(5.9)ND	7.60*	(1.2)ND*	20	(3.1)ND	3	14	45
As	20*	71	(10)ND**	(20)ND	(4.7)ND	38.5*	20.3*	8.1	(163)ND**	4	32	78
Be	(.1)ND**	(0.2)ND	0.360	0.49	1.23*	0.4*	0.33*	0.6	(0.15)ND	5	0.6	59
Cd	23	16	18	16.2	18.6	25.6*	22*	19	24	9	20	17
Ca	74400	47300	65700	63700	68500	57149	69500	72300	69600	8	67600	8.0
Cr	55	54	51	41.7	48.1	51.6	59.7*	57	52	9	52	9.9
Co	7.7	12	9.4	12.7	8.59	10.5*	6.37*	9.9	10	9	10	21
Cu	304	177	254	199	260	274	270	290	267	9	255	16
Fe	18400	11600	15300	15200	18400	13935	17100	18700	18600	9	16400	15
Pb	15900	9490	12100	14600	9870	12300	14400	13700	14900	9	13000	17
Mg	2320	1520	1900	2040	2360	2151	2680*	2840	2430	9	2250	18
Mn	817	476	716	573	680	773	786*	788	804	9	713	17
Mo	8.9	10	(1.5)ND**	(3)ND	(0.86)ND	5.1*	(0.2)ND	2	(1.5)ND	4	6.5	56
Ni	163	127	161	114	143	173	152	166	171	9	152	13
Se	170*	38	(15)ND**	(10)ND	(6.4)ND	(9.4)ND*	(2)ND*	22	(30)ND	3	26	43
Ag	6	1.70	3.4	5.39	(0.4)ND	5.1	5.7	2	3.9	8	4.1	40
Tl	39*	(4.1)ND	110	(20)ND	(4.3)ND	33.1*	(2.4)ND*	(10)ND	(15)ND	3	28	54
V	12	4.9*	9.7	9.8	14.9	10.6*	15.1*	16	13	9	12	29
Zn	1610	1330	1380	1160	1310	1323	1230*	1560	1450	9	1370	11
Ba	3740	5070	4560	5880	3910	5667	7350	5280	5340	9	5200	21
Na	1680	1310	3220	1350	2020	1739	1670	2040	1870	8	1710	16
K	3220	366	296	276	605	395	434*	634*	4950	9	425	31

(continued)

TABLE 9. (continued)

INDUSTRIAL SLUDGE DUPLICATE

ELEMENT	CONCENTRATION (mg/kg) LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	12000	17700	12900	10400	15400	11460	14100	14900	15000	9	13800	17
Sb	16*	50	(10)ND**	(3.5)ND	(5.9)ND	7.60*	(1.2)ND*	23	(3.1)ND	3	16	50
As	(10)ND**	80	(10)ND**	(20)ND	(4.7)ND	31.60*	18.4	11	(41)ND**	3	35	88
Be	(1)ND**	0.5	0.51	0.49	0.153* D	0.4*	0.38*	0.5	0.260	8	0.4	25
Cd	22	16	20	14.2	18.1	25.9*	20	19	20	8	19	18
Ca	73400	55200	68500	54000	68000	54950	69500	67000	73300	9	64900	12
Cr	54	42	50	36.3	44.1	50.5	57*	55	56	9	49	15
Co	7.4	12	9.5	10.8	7.01	10.5*	6.42*	10	11	9	9.4	21
Cu	294	190	296	165	234	272.2	268	292	273	9	254	19
Fe	17000	13400	13200	13200	17700	13470	17100	18200	17500	9	15600	14
Pb	15900	10800	11600	12200	9050	12474	13800	13400	13700	9	12500	16
Mg	2170	1760	1860	1680	2360	2081	2470	2780	2330	9	2170	17
Mn	830	492	627	485	614	733.3	755*	765	826	9	681	19
Mo	7.4	11	(1.5)ND**	(3)ND	(0.86)ND	5.1*	(0.2)ND*	2.3	(1.5)ND	4	6.5	57
Ni	154	130	134	99	135	189*	169*	169	165	9	149	18
Se	(15)ND	45	(15)ND**	(10)ND	(6.4)ND	(4.8)ND*	(2)ND	24	(30)ND	2	34	43
Ag	6.2*	3.1	3.1	4.41	(0.41)ND	5	5.45*	2.1	3.3	8	4.0	35
Tl	52*	(4.1)ND	20	(20)ND	(4.3)ND	27.80*	(2.4)ND	(10)ND	(15)ND	2	24	23
V	11	5.4	9.6	8.82	14	11*	12.1*	16	13	9	11	27
Zn	1580	1180	1360	990	1290	1321	1240*	1500	1530	9	1330	14
Ba	4180	4900	5390	4420	2630	5440	7450	5660	5450	9	5060	26
Na	1680	1460	3130	1200	1940	1623	1690	2050	1820	8	1680	16
K	270	413	321	265	548	355	496*	685*	4900	9	427	33

(continued)

TABLE 9. (continued)

ELECTROPLATING SLUDGE

ELEMENT	CONCENTRATION (mg/kg) LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	4520	4160	4910	3270	5440	4350	5450	6720	7650	9	5110	25
Sb	130	188	142	67.2	88	31.8*	2.4D*	31	120	9	89	69
As	54	66	(10)ND**	24.2D	33.5	66.7*	20.3*	44	(41)ND**	7	44	43
Be	1.3*	(0.2)ND	0.50	0.494	0.15	0.25*	0.35*	(0.12)ND	(0.15)ND	5	0.5	89
Cd	107	110*	112	84.4	115	127*	50.1*	103	156	9	107	27
Ca	53600	41300	51900	48400	32000	38809	50500	51100	56200	9	47100	17
Cr	8220	7370	16500	7060	8190	6834	7550	7180	9050	8	7680	9.7
Co	7.1	11	6.5	16.8	6.3	2.7*	3.3*	5.8	5.2D	7	6.0	42
Cu	796	654	772	602	702	704	730	714	749	9	714	8.3
Fe	30300	28800	27800	27000	33800	24024	29400	32600	33100	9	29600	10
Pb	1250	1150	882	726	1190	1038	810	774	878	9	966	20
Mg	1750	1430	1710	1350	1760	1652	1070*	2180	1970	9	1650	20
Mn	192	205	281*	204	267	364*	116*	259	226	9	235	30
Mo	18*	31	(1.5)ND**	8.89D	22.1	20.8*	4.3	12	(1.5)ND	7	17	54
Ni	502	391	482	349	486	448	159*	474	451	8	416	26
Se	28D	47	(15)ND**	(10)ND	6.4D	(5)ND*	(2.0)ND	(5)ND	(30)ND	3	27	75
Ag	6.4	4.0	(1.5)ND**	5.43	0.4D	5	(2.4)ND**	2.6	2.1D	7	3.6	56
Tl	29D	(4)ND	(10)ND**	(20)ND	4.3D	10D*	(2)ND	(10)ND	(15)ND	3	14	90
V	17*	(0.3)ND	(2.5)ND**	14.8	24.7	16	7.0D	18	(71)ND**	6	16	35
Zn	13500	13400	13100	12400	14700	11680	12900	12900	13400	9	13100	6.3
Ba	50	50	77	52.8	36	95.7	78	34	39	9	57	38
Na	82400	68800	93500	56100	71800	56850	72500	79500	85700	9	74100	17
K	2280	2080	2060	1960	2000	2067	2200	2240	2170	9	2120	5.2

(continued)

TABLE 9. (concluded)

ELECTROPLATING SLUDGE DUPLICATE

ELEMENT	A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
	CONCENTRATION (mg/kg) LABORATORY											
Al	4100	4580	4500	3760	5140	4523	4980	6250	6830	9	4960	20
Sb	126	179	137	67.2	78.4	34*	2.7*	35	124	9	87	67
As	45	66	(10)ND**	(20)ND	25.5	59.7*	19.5*	36	(41)ND**	6	42	44
Be	0.50*	0.20	0.5	0.494	(0.15)ND	0.25*	0.23	0.14	(0.15)ND	7	0.3	52
Cd	110	77	111	80.5	123	132	92	103	121	9	105	18
Ca	52100	34100	50200	47700	34600	38194	46000	50600	55800	9	45500	17
Cr	8220	6440	15900	7110	8500	6965	6850	7100	9800	8	7620	15
Co	6.9	11	6.3	15.8	6.1	6.5*	2.8*	5.9	6.3D	7	7.5	50
Cu	785	522	776	509	718	818.9	660	778	762	9	703	17
Fe	27000	25200	24700	26400	32600	24774	27600	32100	33800	9	28200	13
Pb	1100	865	846	731	1300	955	755	813	798	7	858	14
Mg	1620	1390	1610	1560	1730	1665	1760*	2150	1860	8	1650	8.6
Mn	192	191	226	194	263	361*	218	254	245	8	223	13
Mo	28	30	(1.5)ND**	8.39D	18.3	20.6*	13.4*	12	(1.5)ND	7	19	44
Ni	494	359	457	339	508	458	382	476	438	9	435	14
Se	280*	47	(15)ND**	(10)ND	6.4D	15.4D*	(2)ND	(5)ND	(30)ND	4	24	73
Ag	5.8	3	(1.5)ND**	4.94	0.4D	5	4.8	2.7	2.1D	8	3.6	51
Tl	40*	(4)ND	(10)ND**	(20)ND	4.3D	(9.4)ND*	(2.4)ND	(10)ND	(15)ND	1	4.3	--
V	15	(0.3)ND	(2.5)ND**	12.8	23.6	15	7.15D	18	(71)ND**	6	15	36
Zn	13700	10600	12700	12500	15200	11661	11800	12700	15000	9	12900	12
Ba	61	27	67	46.4	35	89.1	68	69	35	9	55	37
Na	84000	61400	92000	71200	70700	55100	64500	74200	86800	9	73300	17
K	2120	1960	1990	1700	1370	1988	1840*	2230	2230	9	1940	14

TABLE 10. METHOD 3050/6010 SPIKED SOLIDS DATA SUMMARY[a]

RIVER SEDIMENT

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY A	B	C	D	E	F	G	H	I	n[b]	MEAN	%RSD
Al	4730	4710	4720	4420	6820	4984	4580	5570	7790	9	5370	22
Sb	624	912	496	353	555	187*	174	178	600	9	453	56
As	358	341	190	231	188	368*	353*	302	(204)ND**	8	291	26
Be	52	40	45	42	41.9	36*	46.4	48	43	9	44	11
Cd	61	51	54	51	51.9	118*	62.7*	58	52	8	55	8.5
Ca	29800	27200	28400	27200	31200	24100	31000	27000	30050	9	28400	8.1
Cr	30400	30400	31800	27100	66200	27520	29100	27900	37700	7	29200	6.0
Co	60	63	51	92	61.1	68*	55.9*	54	59	9	63	19
Cu	148	126	131	122	121	175*	140	153	146	9	140	13
Fe	87500	85800	70400	67200	112000	82400	83200	85600	99600	9	86000	16
Pb	944	858	868	762	824	856*	915*	884	924	9	871	6.4
Mg	6580	5740	5500	6680	6920	5859	7130	7130	6790	9	6480	9.6
Mn	745	707	549	554	687	745*	737*	716	782	9	691	12
Mo	78	83	(1.5)ND**	52	64.1	67	57.5	62	20	8	60	32
Ni	85	107	70	70	61.6	86*	94.5*	71	(63)ND**	8	81	19
Se	419	324	(15)ND**	297	302	416*	418	449	384	8	376	5.9
Ag	53	40	35	42	35	45	1260*	3.4*	42	7	42	15
Tl	289	177	280	97	209	290*	235*	216	193	8	229	26
V	63	(5.8)ND**	(50)ND**	54	72.8	64	29.8	62	(71)ND**	5	63	11
Zn	1890	1560	1520	1460	1510	1664	1320*	1650	1770	9	1590	11
Ba	102	88	80	83	95.7	105	92.5	102	79	9	92	11
Na	1480	2750	2800	1410	3130	1249	1300	1540	1610	9	1920	39
K	923	842	861	817	1160	1007	988*	1280	1100	9	998	16

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[a] Outlier data are underlined. ND indicates not detected (LOD is given in parentheses). Note that some laboratories reported an "apparent detection limit" in parenthesis that does not correspond to the value that they reported as the IDL (Table 5). A "D" indicates a value between the LOD and LOQ (LOQ=3.33XLOD).

[b] The number of laboratories whose data was used in the calculations of the means and standard deviations.

*Determined by MSAs.

**The LOD value given in parentheses differs from the LOD reported by the corresponding laboratory (Table 5).

(Continued)

TABLE 10. (continued)

RIVER SEDIMENT DUPLICATE

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	4830	6180	3810	3750	6770	4916	4400	5060	7640	9	5260	25
Sb	614	939	641	362	514	198*	170	180	594	9	468	56
As	361	350	171	237	196	315*	302*	301	(204)ND**	8	271	25
Be	53	41	38	43	42.2	59*	45.8	47	43	9	46	14
Cd	61	52	46	52	52.9	115*	54.5*	58	53	8	54	8.3
Ca	29500	28900	23400	27300	30300	22814	28300	27200	30050	9	27500	9.9
Cr	30300	30200	32900	27200	68700	26650	27400	28600	36300	9	34300	39
Co	60	64	58	91	52.9	94*	49.6*	55	61	9	66	25
Cu	147	131	116	123	119	180*	140	153	147	9	140	14
Fe	92000	91300	84600	65600	115000	82800	79300	52000	103000	9	85100	22
Pb	930	890	928	772	814	839*	814*	899	890	9	864	6.5
Mg	6730	6490	5860	6680	6870	5749	6720	7280	6630	9	6560	7.3
Mn	763	729	666	545	656	730*	662*	696	757	8	707	6.1
Mo	78	88	(1.5)ND	54	71.8	67	55.5	59	26	8	62	30
Ni	88	110	79	69	53.4	87*	83.5*	71	(63)ND**	8	80	21
Se	432	401	(15)ND	303	318	434*	410	434	390	8	390	13
Ag	52	41	21	42	26.2*	45	224*	3*	40	7	38	28
Tl	290	173	260	106	193	324*	185*	206	199	9	215	31
V	64	(5.8)ND	(2.5)ND	54	68.7	68	28.4	61	(71)ND**	6	57	27
Zn	1840	1620	1410	1450	1500	1624	1160	1660	1820	9	1560	14
Ba	104	95	90	83	95.7	104	90.5	101	83	9	94	8.6
Na	1480	2880	2820	1400	3130	1253	1290	1550	1590	9	1930	40
K	801	900	706	822	1170	966	871*	1180	1070	9	943	18

(continued)

TABLE 10. (continued)

FLY ASH

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	12600	14400	11600	12100	19100	15977	13000	16300	19900	9	15000	20
Sb	201	171	173	144	96	243*	142	111	142	9	158	28
As	401	431	384	305	248	365*	369*	363	426	9	366	16
Be	56	44	50	45	49.6	54	50.5	50	48	9	50	7.7
Cd	52	42	45	46	48.6	65*	52.3*	47	51	8	48	7.6
Ca	4520	4060	4750	4070	4860	4717	3990*	5300	5510	9	4640	12
Cr	67	67	74	68	78	83	63.7*	74	83	9	73	9.8
Co	62	51	56	49	61.5	71*	54.4*	58	62	9	58	12
Cu	78	67	74	67	75.5	90	72.5	35	86	8	76	11
Fe	24100	17900	11800	8560	41800	27510	15800	24000	34000	9	22800	47
Pb	261	253	240	235	271	312*	273*	293	294	9	270	9.6
Mg	715	653	683	672	870	927	781*	1010	945	9	806	17
Mn	41	81	88	83	107	112	89.4*	99	102	8	95	12
Mo	82	85	36	67	62	85*	69	68	58	9	68	23
Ni	76	75	69	62	74.5	85	72.7*	76	84	9	75	9.4
Se	425	435	384	385	330	248	345	360	398	8	383	9.6
Ag	54	24	45	42	(0.4)ND	50	74.4*	3.5	41	8	37	50
Tl	258	55	165	104	122	222	206*	232	206	9	174	39
V	122	95	109	109	141	138	116	131	133	9	122	13
Zn	112	84	88	95	120	113	98.6	110	102	9	102	12
Ba	720	680	706	612	765	761	640	716	718	9	702	7.2
Na	720	911	442	711	1410	652	615	801	790	9	784	34
K	2080	1900	1970	1980	2820	2406	1930*	2720	2880	9	3200	18

(continued)

TABLE 10. (continued)

FLY ASH DUPLICATE

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	12800	19100	12400	11800	17900	16062	13300	15500	19100	9	15300	19
Sb	187	146	155	147	93	203*	148	123	143	9	149	22
As	385	471	378	308	280	365*	347	366	441	9	371	16
Be	56	45	51	44	50.5	53	51.5	50	48	9	50	7.5
Cd	53	42	42	46	49.4	59*	51.9*	47	53	9	49	11
Ca	4440	4260	4870	3800	4720	4894	3700*	5230	5360	9	4590	13
Cr	70	71	74	66	77.5	83	62.6*	72	83	9	73	9.6
Co	62	52	55	48	59	69*	51.8	57	62	9	57	11
Cu	79	70	75	66	75.5	89	77	84	89	9	78	10
Fe	21500	22100	13400	8910	37200	28120	15200	20900	31700	9	22100	41
Pb	268	254	245	233	274	309*	269*	246	302	9	267	9.6
Mg	705	698	745	602	835	946	678*	970	915	9	788	17
Mn	47	86	90	81	94.5	111	85.5	96	101	8	93	10
Mo	83	86	36	67	62.5	89*	69	69	58	9	69	24
Ni	78	80	76	61	73	85	71.8*	75	87	9	76	10
Se	417	457	375	380	337	460*	388	361	409	9	398	10
Ag	54	15	46	43	(0.4)ND	51	60.2*	4.7	41	8	39	49
Tl	260	37	162	104	128	228	212*	228	191	8	189	29
V	122	100	115	106	137	138	116	129	133	9	122	11
Zn	113	91	89	93	114	113	96.5*	108	106	9	103	10
Ba	744	740	653	602	730	758	680	716	710	9	704	7.2
Na	725	1050	442	677	1260	658	650	789	790	9	782	31
K	2040	2080	1910	1840	2670	2294	1890	2620	2790	9	2240	17

(continued)

TABLE 10. (continued)

ESTUARINE SEDIMENT

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	13200	21600	12200	13500	18500	15235	14200	18400	21400	9	16500	22
Sb	131	95	42	37	74.8	107*	26.8	13	63	9	66	61
As	257	316	215	189	174	238*	253*	248	334	9	247	21
Be	54	40	45	43	44.4	50	48.5	48	46	9	47	8.9
Cd	53	41	42	44	45.2	54*	53.7*	50*	50	9	48	11
Ca	3620	3160	3530	3350	3970	3378	2980*	4130	4120	9	3580	12
Cr	77	78	77	76	78.4	86	86.4*	84	92	9	82	6.9
Co	60	45	45	47	50.4	54	57.8*	53	54	9	52	10
Cu	63	51	52	54	50.3	64	58.5	65	59	9	57	10
Fe	26600	23300	20900	22800	26700	23680	25600	27600	29000	9	25100	10
Pb	268	242	198	225	252	287*	253*	275	280	9	253	11
Mg	8060	7260	6760	7470	8140	7435	8050	9340	8290	9	7870	9.5
Mn	218	224	233	240	275	284	271*	295	263	9	256	11
Mo	57	51	(1.5)ND**	39	41	50*	46.6*	45*	33	8	45	17
Ni	73	72	61	60	57	74*	71.8*	74*	68	9	68	9.9
Se	419	425	308	367	343	425	414	391	394	9	387	11
Ag	54	25	40	41	5.1	49	216*	6	42	6	42	24
Tl	254	107	194	95	222*	266*	229*	230	201	9	200	30
V	86	62	73	77	86	86	88.2*	91	91	9	82	12
Zn	166	122	131	141	204	146	152*	149	138	8	143	9.4
Ba	84	73	66	69	82.4	89	76.5	86	85	9	79	10
Na	11200	9490	9890	10700	10300	9090	9100	11600	11300	9	10300	9.3
K	3710	3340	3450	3550	4240	3644	3200*	5040*	4660	9	3870	16

(continued)

TABLE 10. (continued)

ESTUARINE SEDIMENT DUPLICATE

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	13200	37800	12900	13400	19500	15345	13800	20000	21400	8	16200	22
Sb	129	154	43	32	74.3	120*	29.4	33	60	9	75	64
As	262	521	209	187	179	275*	245	239	341	8	242	22
Be	55	64	46	43	45.2	51	50.5	46	46	9	50	13
Cd	54	63	40	45	65.3	60*	48.9*	50*	51	9	53	16
Ca	3660	5090	3590	3490	4070	3522	3500	4130	4220	8	3770	8.3
Cr	77	123	75	77	78.9	90	79	84	90	8	81	7.3
Co	61	37	47	49	50.5	55	55.4*	51	55	8	53	8.4
Cu	64	80	53	53	50.7	64	59.5	63	60	8	58	9.3
Fe	29100	39100	21000	23000	29000	20155	25200	27000	28500	9	26900	21
Pb	273	379	205	227	258	280*	253*	269	282	8	256	11
Mg	8260	11900	6560	7520	8240	7430	7950	8740	8180	8	7860	8.6
Mn	219	356	236	240	275	290	252	286	272	8	259	10
Mo	59	99	(1.5)ND**	39	41	52*	43.7	45*	34	7	45	19
Ni	74	118	60	61	58	77*	70.5*	73*	69	8	68	11
Se	418	799	318	370	353	433	429	381	408	8	389	10
Ag	55	61	42	42	17.2	49	38.6	6	41	9	39	45
Tl	257	149	170	92	186	246*	224	218	190	9	192	27
V	87	99	74	77	86.5	88	83	90	92	9	86	8.8
Zn	169	193	131	142	205	150	152*	148	140	9	159	16
Ba	84	117	66	70	83.5	89	78	86	85	9	84	17
Na	11400	15300	10100	10900	11000	8940	9100	11400	11100	8	10500	9.5
K	3730	6000	3300	3480	4310	3490	3900*	4840*	4640	9	4200	19

(continued)

TABLE 10. (continued)

MINE TAILING

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	13000	22900	11700	11500	15000	12330	15200	17000	20000	9	15400	26
Sb	73	87	25	17	50	40*	(5)ND	14	30	8	42	63
As	1080	858	973	664	549	865	1290*	913	938	9	903	24
Be	48	38	41	37	46.4	56*	29*	48	43	9	43	18
Cd	50	38	37	37	47.6	56*	39.9*	43	61	9	46	19
Ca	9800	9500	8750	9970	10800	9395	8290*	10400	11800	9	9860	11
Cr	58	94	79	45	(0.46)ND	87*	53.5	58	57	8	66	27
Co	56	42	47	42	52.8	59*	31.1*	54	49	9	48	18
Cu	314	245	267	228	284	297	308	317	87	8	282	12
Fe	10000	10800	8020	7340	12200	8180	10400	10600	12600	9	10000	18
Pb	6170	5680	6150	5750	5690	6100	3770*	6310	6250	8	6010	4.4
Mg	14600	13900	13200	13100	15000	12820	14000	16400	16600	9	14400	9.6
Mn	99800	93500	102000	82400	80500	94850	92800	86500	105000	9	93000	9.2
Mo	112	120	68	69	105	102*	81.5*	94	85	9	93	20
Ni	68*	68	64	49	66.5	69*	42.2*	66	72	9	63	16
Se	433	465	335	346	380	392*	403*	350	289	9	377	14
Ag	56	25	54	39	11.6	66	44.2*	0.54	49	9	38	57
Tl	432	114	335	199	(4.3)ND	217*	148*	217	(247)ND**	7	237	46
V	66	37	41	47	44.3*	67	41.7*	63	41	9	50	24
Zn	452	371	380	349	548*	480*	275*	470	412	9	415	20
Ba	498	494	423	345	480	518	438	479	448	8	472	6.9
Na	4140	4150	3800	3440	3730	3342	3320	4370	4510	9	3870	12
K	7850	8260	7140	6360	7890	7245	7220*	9060	10300	9	7930	15

(continued)

TABLE 10. (continued)

MINE TAILING DUPLICATE

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	12900	22500	11200	13200	14600	10985	14800	17100	21100	9	15400	27
Sb	53	79	19	20	46.7	40*	(5)ND**	14	29	8	40	54
As	1080	798	928	659	528	850	850	941	964	9	844	20
Be	48	36	42	36	43.1	55*	44.5	47	44	9	44	13
Cd	50	35	39	37	46.2	59*	42.4	42	59	9	46	20
Ca	9550	8360	9060	9770	10700	9185	7410*	10400	11500	9	9550	13
Cr	57	89	81	46	(0.46)ND	47*	53	59	58	8	61	25
Co	55	39	48	42	49.8*	50*	29.9*	53	49	9	46	17
Cu	309	223	265	227	268	299	300	315	87	8	276	13
Fe	9440	10200	8000	8460	11700	7290	10000	10900	12800	9	9870	18
Pb	6280	5200	6620	5750	5800	6118	3520*	6220	6230	8	6030	7.2
Mg	14500	12900	13100	13700	15000	12240	14000	16600	16600	9	14300	11
Mn	101000	84400	104000	79200	91300	90550	93000	86500	105000	9	92800	9.7
Mo	113	107	69	68	95.9	241*	77.4*	67	84	8	85	21
Ni	65	64	65	49	68.9*	80*	42*	66	68	9	63	18
Se	435	435	356	340	350	392*	768*	347	229	7	379	11
Ag	56	23	55	40	11.6	66	44.4	0.54	48	8	43	42
Tl	427	137	297	205	(4.3)ND	207*	144*	208	(247)ND**	7	232	43
V	65	34	43	46	62	58	65.6*	64	41	9	53	23
Zn	450	338	392	360	451	494*	259*	471	423	9	404	19
Ba	496	444	420		466	525	432	481	460	8	466	7.4
Na	4030	3840	3890	3430	3800	3361	3160	4330	4490	9	3810	12
K	7700	7480	6970	6780	8040	6250	6650*	9120	9840	9	7650	16

(continued)

TABLE 10. (continued)

HAZARDOUS WASTE #1

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	5440	7640	4760	5190	7400	5815	6660	6910	7400	9	6370	17
Sb	160	151	114	99	142	243*	108	52	131	8	120	29
As	274	254	203	195	189	256*	230	230	249	9	231	13
Be	52	39	42	41	29.6	56.5*	46.2	51*	43	9	44	18
Cd	52	37	40	42	31.6	43	54*	46	44	9	43	16
Ca	80200	75000	74200	72500	81900	62100	72200	73800	78800	8	76100	4.9
Cr	151	126	140	128	90.6	151.1	167*	152	155	8	146	9.6
Co	57	41	47	45	32.7	65.5*	59.5*	57*	50	9	51	20
Cu	239	142	195	169	127	218.4	200	205	205	9	189	19
Fe	20000	18800	15400	16500	22800	16325	19900	19900	21100	9	19000	13
Pb	452	367	350	381	142	508*	446*	465*	350	8	415	15
Mg	27400	25900	23400	25600	28000	24320	24600	26600	25200	9	25700	5.8
Mn	384	337	359	343	281	465*	448*	399	367	9	376	15
Mo	60	49	3.2	38	57.0*	64.5*	54.1*	48	39	8	51	19
Ni	67	62	60	54	37.6	78.5*	76.8*	68*	60	9	63	20
Se	425	391	263	263	370	412.5*	403	379	404	9	368	17
Ag	52	37	43	42	36	58.2*	43.7*	1.8	42	8	44	17
Tl	247	149	209	170	209*	234.4*	188	203	178	9	199	16
V	88	44	52	57	42.8	77.5*	59.5	71	61	9	59	20
Zn	233	165	190	192	154	250.8*	244*	222	200	9	206	17
Ba	237	215	199	182	212	237.3	217	209	205	9	213	8.2
Na	700	910	632	683	1060	706.5	650	750	727	7	693	6.0
K	1100	1160	965	1020	1400	12	1100	1610	1400	8	1220	18

(continued)

TABLE 10. (continued)

HAZARDOUS WASTE #1 DUPLICATE

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY									n	MEAN	%RSD
	A	B	C	D	E	F	G	H	I			
Al	5220	5690	4670	4930	7840	5935	6160	6620	7090	9	6020	17
Sb	153	148	125	101	139	294*	102	64	137	8	121	25
As	267	265	211	182	200	253*	238	228	255	9	233	13
Be	52	40	42	41	42.8*	59*	47.2	50*	44	9	46	13
Cd	52	37	39	42	42.1*	45	48	45	44	9	44	10
Ca	77100	75900	73000	72500	58500*	60850	72700	73800	78100	9	71400	9.7
Cr	150	129	145	133	155	149	138	149	152	9	144	6.2
Co	56	42	47	45	45.3*	67*	48	57*	50	9	51	15
Cu	200	175	178	172	196	198	195	268	186	8	188	6.0
Fe	19500	17700	15600	15900	24100	16135	19100	20500	22500	9	19000	16
Pb	437	361	366	385	279*	5*	410	467*	379	8	386	15
Mg	26500	25500	24100	25600	21800*	23875	24400	26500	25600	9	24900	6.0
Mn	381	6470	386	353	442	491*	363	402	358	8	397	12
Mo	63	48	(1.5)ND**	41	49.2	63*	45.8	48	37	8	49	19
Ni	67	61	61	58	61.1*	84*	61	70*	61	8	62	6.9
Se	410	394	274	348	370	458*	409	381	386	8	394	8.3
Ag	52	35	43	43	32	58*	34.4	3.9	43	8	43	21
Tl	243	151	204	179	173	305*	192	199	184	9	203	22
V	64	43	52	57	63.1*	74*	60	71	63	9	61	16
Zn	223	192	186	195	237	250*	214	224	196	9	213	10
Ba	234	203	204	184	218	246	213	217	206	9	214	8.5
Na	704	874	493	713	1060	741	630	734	747	9	744	21
K	1060	1080	962	1040	1440		985	1570	1360	8	1190	20

(Continued)

TABLE 10. (continued)

INDUSTRIAL SLUDGE

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	13900	10100	10300	12600	15600	12050•	15700	15300	14500	9	13300	16
Sb	122	116	103	57	120	127•	60.5	65	103	9	98	28
As	252	229	220	174	195	312•	234	238	307	9	240	19
Be	51	29	42	33	39.9	49•	47.6	48	46	9	43	18
Cd	68	41	62	51	56.3	78	65.5	64	69	9	62	18
Ca	75700	44600	63600	64600	66500	55850•	80000•	68700	72200	9	65800	16
Cr	102	68	89	77	82.4	117	115	99	105	9	95	18
Co	56	36	48	39	47	53	60.4•	56	57	9	50	17
Cu	356	191	294	222	208	321	314	331	324	9	293	18
Fe	18600	11000	13900	15700	17500	13735	19200	18000	16700	9	16000	17
Pb	17000	10000	15200	16200	10300	12960	17600•	14700	14800	9	14300	19
Mg	2290	1370	19400	2040	2260	2092•	1630•	2790	2300	9	2090	20
Mn	890	436	678	583	716	798•	868	794	815	9	731	20
Mo	56	39	8.30	39	41.2	58•	40.4•	42	36	8	44	19
Ni	205	138	105	147	189	244•	251	218	214	9	199	20
Se	404	293	296	314	284	433	376	364	369	9	348	15
Ag	60	15	47	38	38.1	54•	47.5•	4.6	48	9	39	46
Tl	251	129	216	250	181	300	239	219	186	8	230	17
V	63	28	38	63	53.2	55	54.5•	61	56	9	52	23
Zn	1700	904	1370	1700	1300	1370	1170	1520	1640	9	1410	19
Ba	4060	4230	5470	4060	4790	5405	8200	5390	4910	8	4790	13
Na	2170	1460	3040	2170	2300	2163	2130•	2530•	2410	9	2270	18
K	749	508	763	749	1010	899	758	1220	908	9	849	22

(continued)

TABLE 10. (continued)

INDUSTRIAL SLUDGE DUPLICATE

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	13800	11100	12400	12400	15200	11470	14000	14700	13900	9	13200	11
Sb	125	98	90	71	147	123*	69*	68	102	9	99	28
As	262	203	227	177	223	315*	238	238	321	9	245	20
Be	50	27	44	32	42.6	48*	49.1	47	47	9	43	19
Cd	69	35	60	48	67.5	81*	71.7	63	70	9	63	20
Ca	75300	42800	63600	63900	70600	55250	69000	69200	68700	8	66900	9.0
Cr	102	59	89	76	87	112*	109*	98	106	9	93	19
Co	56	32	45	40	55.2	55	57.4*	55	56	9	50	18
Cu	352	168	303	215	300	317	324	314	320	9	290	20
Fe	18600	9840	13400	15600	17200	13540	17200	18100	17400	9	15700	18
Pb	17100	7820	13800	16000	10400	13104	15400	14700	14300	9	13600	21
Mg	2240	1220	18400	2030	2380	2061	2260*	2780	2340	8	2240	13
Mn	905	399	675	583	757	765*	828	808	840	8	770	13
Mo	55	36	2.40	39	49.9	49*	40.8	41	36	8	43	16
Ni	204	125	178	146	199	243*	227*	212	220	9	195	20
Se	422	273	291	317	306	385*	398	350	389	9	349	15
Ag	48	13	49	38	34.6	50	43.2	4.8	48	7	44	14
Tl	256	123	203	84	196	307*	213*	210	203	7	227	18
V	63	26	49	42	56.8	52	55.5	60	57	8	54	12
Zn	1700	884	1360	1150	1400	1361	979*	1530	1560	9	1320	21
Ba	3800	4160	4490	6320	4720	5150	6900	5580	4880	9	5110	20
Na	2100	1280	3440	1710	2570	2454	2160	2510	2380	8	2420	21
K	749	501	687	681	1010	899	920	1080*	872	9	822	22

(Continued)

TABLE 10. (continued)

ELECTROPLATING SLUDGE

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	5010	6430	4280	4410	6000	4682	4940	5980	7050	9	5420	18
Sb	304	405	304	160	237	221*	139	146	152	9	230	40
As	279	297	226	197	211	344*	273	284	280	9	266	17
Be	47	38	44	25	41.7	42	45	38	44	8	42	7.6
Cd	148	119	139	91	159	174*	146	156	178	9	146	19
Ca	52600	47500	48300	48300	35800	37920	50000	50400	54200	9	47200	13
Cr	8160	7620	8210	7210	5740	6745	7620	7050	9470	9	7540	14
Co	53	47	44	36	47.8	58*	26*	50	51	9	46	21
Cu	842	811	809	432	799	866	755	756	807	8	806	4.7
Fe	33300	11000	23400	28400	33300	25860	30700	32600	35200	8	30300	14
Pb	1530	1450	1280	731	1220	1223	899*	1140	1310	9	1200	21
Mg	1730	1600	1510	1730	1810	1669	1610*	2100	1930	9	1740	10
Mn	229	250	265	175	318	260	185*	297	271	9	250	19
Mo	101*	85	(1.5)ND**	46	58	71*	50.8*	51	33	8	62	53
Ni	541	436	600	285	514	507	8.4*	514	483	7	514	9.8
Se	401	439	287	353	301	467*	464	402	413	9	392	17
Ag	38	36	47	26	2.09	21*	43	6	44	7	36	27
Tl	242	136	186	82	151	41*	363*	213	184	9	178	53
V	63	21	28	36	64.1	56	47.8*	59	72	9	50	36
Zn	13800	12900	12800	12700	12700*	11315	13800	12700	15400	9	13100	8.5
Ba	49	49	61	48	32.2	58	48.2	61	35	9	49	21
Na	82400	4680	93300	80700	71200	56400	71400	74300	86000	8	77000	15
K	2690	2520	2400	1700	2550	2509	2200	2710	2720	8	2540	7

(continued)

TABLE 10. (concluded)

ELECTROPLATING SLUDGE DUPLICATE

CONCENTRATION (mg/kg)

ELEMENT	LABORATORY A	B	C	D	E	F	G	H	I	n	MEAN	%RSD
Al	4730	5860	4280	4680	6670	4828	4020	5160	7010	9	5340	18
Sb	295*	389	320	177	227	221*	132	149	152	9	229	39
As	303	302	229	196	205	344*	178*	278	294	9	259	22
Be	45	38	43	31	43.8	44	44.4	38	43	8	42	6.5
Cd	141	119	140	112	144	173*	116*	149	181	9	142	17
Ca	51100	43800	51300	48400	35400	38740	49600	48600	55900	9	47000	14
Cr	8220	7300	8240	7210	7790	6905	7510	7020	9430	9	7740	10
Co	51	47	45	44	48.6	59*	25.1*	50	51	7	48	5.9
Cu	873	757	833	553	707	890	710	763	804	9	766	14
Fe	32600	29400	24200	27300	40100*	25960	30400	30200	33200	9	30400	15
Pb	1480	1330	1310	933	1050	1267	882*	1160	1270	9	1190	17
Mg	1760	1600	1540	1800	1980	1681	1560*	1990	1970	9	1760	10
Mn	213	248	263	223	293	305	162*	291	273	9	252	18
Mo	78	92	(1.5)ND**	46	50.5	80*	48.6*	51	35	8	61	33
Ni	555	423	559	355	466	525	265*	501	492	9	460	21
Se	383	429	258	352	299	467*	454	413	427	9	387	18
Ag	52	30	44	36	(0.41)ND	65*	252*	5.5	44	6	45	27
Tl	224*	136	190	85	148	306*	199*	210	191	9	188	33
V	67	21	27	45	66.2	57	23.6	59	74	9	49	42
Zn	13600	11900	13300	12700	13900	11505	13700	12300	14700	9	13100	7.9
Ba	64	27	60	61	32.9	97	80	54	38	9	57	40
Na	81200	66100	94500	81500	73300	57900	66000	74300	85300	9	75600	15
K	2510	2570	2570	2150	2490	2530	1810*	2700	2800	7	2600	4.4

TABLE 11. METHOD 3050/6010 QC SOLUTION DATA SUMMARY[a]

	CONCENTRATION (ug/L) LABORATORY													
ELEMENT	A	B	C	D	E	F	G	H	I	TARGET VALUE	n^b	MEAN	%RSD	MEAN/ TARGET
Al	9630	14200	9710	9150	10000	9900	9350	9920	10380	10000	8	9760	4.0	0.98
Sb	9920	1370	11400	9780	8750	10400	9460	10400	10000	10000	8	10000	7.7	1.00
As	10100	12000	11000	8360	8110	10100	9260	10000	8730	10000	9	9740	13	0.97
Be	2520	3270	2530	2100	2410	2460	2390	2350	2520	2500	7	2450	2.9	0.98
Cd	2520	3120	2410	2260	2580	2610	2240	2480	2935	2500	9	2570	11	1.03
Ca	10200	13200	9200	8840	10200	10100	9410	10900	10100	10000	8	9870	6.7	0.99
Cr	2540	4570	2590	2340	2480	2700	2300	2460	2432	2500	8	2480	5.2	0.99
Co	2520	3170	2390	2290	2440	2550	2260	2440	2345	2500	8	2400	4.3	0.96
Cu	2450	3190	2390	2050	2475	2390	2280	2410	2383	2500	7	2400	2.6	0.96
Fe	10400	16600	10000	9020	10000	10600	9380	10100	9670	10000	8	9900	5.3	0.99
Pb	10100	13500	9290	9720	9710	10100	8840	9700	8670	10000	8	9520	5.6	0.95
Mg	9630	13500	9420	8890	9480	10000	8760	10600	9400	10000	8	9520	6.2	0.95
Mn	2420	151	2425	2220	2470	2560	2370	2440	2275	2500	8	2400	4.5	0.96
Mo	2520	2780	2320	2270	2150	2580	2350	2440	2110	2500	9	2390	8.9	0.96
Ni	2510	3980	2575	2140	2420	2570	2280	2510	2589	2500	8	2450	6.6	0.98
Se	10200	14400	11200	9080	8210	10700	9390	9520	9000	10000	8	9660	10	0.97
Ag	1240	(0.8)ND	1630	1100	986	2670	544	ppt.*	1040	2500	7	1320	51	0.53
Tl	9620	9170	11100	8480	1250	9720	8410	9190	8610	10000	8	9290	9.5	0.93
V	2420	2800	2280	2110	2370	2570	2280	2410	2252	2500	9	2390	8.4	0.96
Zn	2510	3060	2200	2270	2470	2419	2250	2430	2046	2500	8	2320	6.8	0.93
Ba	2500	3640	2440	2110	2650	2510	2360	2460	2270	2500	8	2410	6.8	0.96
Na	9780	13610	17300	9550	10100	10200	8750	10400	9400	10000	7	9740	5.8	0.97
K	9010	13400	8840	9100	10200	10100	8530	10200	9900	10000	8	9490	7.2	0.95

[a] Outlier data are underlined. ND = not detected (the value reported, which is not the IDL, is in parentheses).
[b] The number of laboratories whose data was used in the calculations of the means and standard deviations.
*Reported as precipitated.

SECTION 6

DISCUSSION

The experimental results presented in Section 5 were used to establish the precision and accuracy of Method 6010 and of Method 3050/6010. Both the precision and accuracy performance parameters are examined element by element and matrix by matrix in this Section. The data for Method 3050/6010 are examined in order to determine the contributions of the digestion procedure and of the ICP-AES measurement procedure to the overall method variance. In addition, instrumental detection limits, the method of standard additions, the results of sequential versus simultaneous ICP instruments, and a comparison of the ICP-AES results with atomic absorption spectroscopy results are discussed. The results obtained by Method 3050/6010 are compared to the true values of the three NBS SRM's and an EPA CLP reference material that were used in this study.

INSTRUMENT DETECTION LIMITS

The participating laboratories reported a very wide range of IDL's for many of the target elements, a factor of 10 or more. For example, the Method 6010 "Estimated IDL" for arsenic is 53 µg/L and this study required IDL 200 µg/L. However, in this study the reported range of IDL's for arsenic is 22-400 µg/L, and the average IDL is 139 µg/L. Two laboratories reported IDL's for arsenic below the "Estimated IDL", six reported IDL's above the "estimated" value, and one laboratory reported an IDL that was about the same as the "estimated" value. For sodium, the "Estimated IDL" is 29 µg/L, the reported range is 13-4940 µg/L, and the mean is 930 µg/L. The actual average IDL found in this study for sodium is thus over 30 times the "Estimated IDL" given in Method 6010. Moreover, Table 6 shows that for all elements the average of the reported IDL's is greater than the "Estimated IDL" that is given in Method 6010. We provide UNLV "Recommended Required" IDL's in Table 6, that were obtained by inspection of the mean, "Estimated," and minimum IDL's that are given in the table. In general, half of the participating laboratories reported values at or below the UNLV "Recommended Required" IDL's.

PRECISION

Precision is a measure of agreement between individual determinations of the 23 target elements under the experimental conditions of Method 6010 or Method 3050/6010. The percent relative standard deviation (percent RSD) of the mean concentrations reported in Tables 7, 8, 9, 10, and 11 can be used as an estimate of the precision.

Method 6010

The percent RSD data for the Method 6010 QC solutions and the Method 6010 spiked bulk digests were used as an estimate of the precision of Method 6010.

Method 6010 QC Solutions--
The results of the analyses of these interference-free blind QC solutions are given in Table 8, and the target elements are listed in order of decreasing percent RSD (i.e., increasing precision) in Table 12. Together, these two solutions contained all 23 elements at concentrations greater than 100 times the Method 6010 "Estimated IDL's." The measurement precision of the 23 elements by Method 6010 is excellent, as illustrated by the percent RSD's, which are less than 10 percent. The percent RSD for silver is the highest, 9.1 percent, and that for barium is the lowest, 3.1 percent. The median (middle value) percent RSD for Method 6010 is 6.5 percent. Thus, under these constraints of concentration and matrix, the measurement of the 23 target elements by Method 6010 is excellent. For comparison, the percent RSD's for elements in the Method 3050/6010 QC solutions, which are also excellent, are listed in Table 8. They will be discussed later.

Method 6010 Performance Evaluation Materials, The Spiked Bulk Digests--
The interlaboratory precision for Method 6010, with digestion eliminated as a variable, was determined for the 23 elements in the spiked bulk digests of six representative solid complex matrices, including river and estuarine sediments and industrial sludges (Table 7). The analyte concentrations in these spiked bulk digests were about 100 times the instrumental detection limits. The percent RSD's for each of the 23 elements in the spiked bulk digests are found in Table 13. The median percent RSD's for the 6 sediments, across the 23 elements, range from 6.8 percent to 11 percent. Thus, the precision for the measurement of the target elements in these complex solutions is very good.

The seventh spiked bulk digest, from coal fly ash, was spiked with very high levels of molybdenum and vanadium (0.1

TABLE 12. PRECISION VALUES FOR THE MEASUREMENT OF THE 23 TARGET ELEMENTS BY METHOD 6010 IN THE QUALITY CONTROL SOLUTIONS

Method 6010[a]		Method 6010 with Method 3050[b]	
Element	%RSD[c]	Element	%RSD[c]
Ag	9.1	Ag	51
Tl	8.5	As	13
Zn	8.3	Cd	11
Cr	8.2	Se	10
Sb	7.7	Tl	9.5
Se	7.5	Mo	8.9
Ca	7.4	V	8.4
Cd	7.0	Sb	7.7
Mo	6.9	K	7.2
K	6.6	Zn	6.8
V	6.6	Ba	6.8
Mg	6.5	Ca	6.7
As	6.4	Ni	6.6
Al	6.3	Mg	6.2
Co	5.9	Na	5.8
Fe	5.9	Pb	5.6
Pb	5.9	Fe	5.3
Be	5.8	Cr	5.2
Ni	5.7	Mn	4.5
Cu	5.6	Co	4.3
Mn	4.3	Al	4.0
Na	4.2	Be	2.9
Ba	3.1	Cu	2.6

[a]. The median percent RSD is 6.5 percent.

[b]. The median percent RSD is 6.7 percent.

[c]. The percent RSD data are presented in order of increasing precision.

TABLE 13. PERCENT RSD's FOR THE DETERMINATION OF THE 23 TARGET ELEMENTS IN THE SPIKED BULK DIGESTS

ELEMENTS	HAZARDOUS WASTE 1	RIVER SEDIMENT	FLY ASH	ESTUARINE SEDIMENT	INDUSTRIAL SLUDGE	ELECTRO-PLATING SLUDGE	MINE TAILING
Al	11	19	16	1.9	11	13	7.6
Sb	5.6	52	73	8.7	3.2	24	4.4
As	13	11	83	22	25	8.6	5.3
Be	5.8	5.8	57	4.8	6.4	9.9	8.5
Cd	11	6.6	5.7	7.6	3.1	9.8	12
Ca	8.8	9.4	5.6	5.3	8.5	7.0	7.9
Cr	6.2	5.5	36	7.6	5.8	7.8	39
Co	11	14	21	6.8	6.7	11	15
Cu	4.4	4.3	9.7	6.0	11	7.8	12
Fe	6.6	8.3	8.8	6.0	6.9	8.4	8.4
Pb	15	7.2	22	4.7	3.9	5.6	8.0
Mg	8.8	8.1	15	9.4	8.0	20	10
Mn	10	13	14	11	11	9.6	5.5
Mo	20	33	19	28	16	36	21
Ni	9.4	8.9	8.1	5.4	5.1	9.2	12
Se	7.5	13	16	6.2	13	13	19
Ag	44	23	17	46	47	19	27
Tl	19	13	22	29	30	20	29
V	12	58	7.5	7.3	5.5	11	18
Zn	9.1	6.7	7.6	15	10	2.5	16
Ba	11	10	8.7	6.4	8.0	20	11
Na	17	38	49	4.7	5.8	9.8	7.9
K	8.8	7.4	4.2	4.8	13	5.8	7.9
MEDIAN PERCENT RSD	10	10	16	6.8	8.0	11	11

percent). The percent RSD's for the determination of the 23 elements in this spiked digest range from 4.2 percent to 83 percent with a median of 16 percent. It is not apparent from the results whether Mo, V, or both of the elements cause chemical, physical, or spectral interferences, but the addition of these two elements significantly decreased the measurement precision of many of the 23 target elements. It should be noted that the percent RSD for vanadium is very high in the fly ash spiked bulk digest. Two laboratories reported it as "not detected," and one laboratory reported it as below the limit of quantitation (LOQ, 3.33 times the IDL), even though it was present at a concentration of 0.1 percent.

The median percent RSD's for the 23 target elements, across the 7 spiked bulk digests, are given in Table 14 in order of decreasing percent RSD (i.e., increasing precision of measurement by Method 6010). Beryllium has the lowest median percent RSD of 6.4 percent, and Mo, Ag, and Tl have the highest, over 20 percent. Fourteen of the 23 target elements have median percent RSD's of less than or equal to 10 percent, and this treatment of the percent RSD data suggests that these elements are measured very reproducibly by Method 6010.

Method 3050/Method 6010

Method 6010 requires sample digestion to produce a solution that is suitable for analysis by ICP spectroscopy. The precision of the combination of Method 6010 with the digestion Method 3050 was estimated from the data for the unspiked and spiked solids in Tables 9 and 10. Analysis of the data from the Method 3050/6010 spiked solids and the data from the Method 6010 spiked bulk digests allows the variances which are due to digestion and to the spectroscopic measurement to be separated. Each participating laboratory determined the percent solids on a portion of each of the 7 Method 3050/6010 performance evaluation solids. The results which are given in Table 15 indicate that the moisture content was negligible.

Method 3050/6010 QC Solutions--

The two Method 3050/6010 QC solutions were digested according to Method 3050 and were analyzed by Method 6010. Like the Method 6010 QC solutions, they contained all of the 23 target elements in concentrations of about 100 times the Method 6010 "Estimated IDL's."

The results for the Method 3050/6010 analysis of these two QC solutions are presented in Table 11. The elements are listed in Table 12 in order of decreasing percent RSD or increasing precision. With the exception of silver (percent RSD=51), the precisions of the other 22 elements are excellent

TABLE 14. SUMMARY OF METHOD 6010 ELEMENTAL PRECISION (IN TERMS OF MEDIAN PERCENT RSD)[a] FOR THE 23 ELEMENTS ACROSS THE SPIKED BULK DIGESTS AND THE SPIKED SOLIDS

Method 6010 Spiked Bulk Digests		Method 3050/6010 Spiked Solids	
Element	Average %RSD	Element	Average %RSD
Ag	27	Sb	40
Tl	22	Ag	30
Mo	21	Tl	28
As	13	Al	20
Se	13	Mo	20
V	11	As	20
Co	11	Fe	18
Al	11	V	18
Mn	11	K	18
Ba	10	Co	18
Na	9.8	Ni	15
Mg	9.4	Na	15
Zn	9.1	Cd	14
Ni	8.9	Be	13
Sb	8.7	Zn	13
Ca	8.5	Se	12
Fe	8.3	Cu	12
Cu	7.8	Ca	12
Cd	7.6	Cr	12
Cr	7.6	Mn	11
Pb	7.2	Pb	11
K	7.4	Mg	10
Be	6.4	Ba	9.8

[a] Smaller median percent RSDs suggests higher precision. These data are presented in order of increasing precision. The median percent RSDs were determined for each element for all of the valid data across the seven matrices.

TABLE 15. PARTICIPATING LABORATORIES PERCENT SOLIDS DETERMINATION DATA SUMMARY*

Sample	Laboratory								Mean	Std Dev	Range
	A	B	C	D	E	G	H	I			
River Sediment	97.7	97.9	98.6	99.0	98.25	99.87	98.5	98.	98.5	0.6	97.7 - 99.9
Coal Fly Ash	99.8	99.8	99.8	99.5	100.00	99.97	99.3	100.	99.8	0.2	99.3 -100.0
Estuarine Sediment	98.0	98.3	99.6	98.3	98.25	99.92	98.4	98.	98.6	0.6	98.0 - 99.9
Mine Tailing	98.8	97.4	99.3	93.5	97.49	99.87	98.0	97.	97.7	1.6	93.5 - 99.9
Hazardous Waste 1	98.0	99.3	99.7	99.8	98.2	99.94	99.5	99.	99.2	0.7	98.0 - 99.9
Industrial Sludge	96.8	97.1	99.0	98.0	97.75	99.84	97.7	98.	98.0	0.8	96.8 - 99.8
Electroplating Sludge	97.2	97.7	98.8	98.8	98.25	99.87	98.1	98.	98.3	0.7	97.2 - 99.9

* Laboratory F did not report percent solids data.
The values are given as reported by the laboratories.

with percent RSD's equal to or less than 13 percent. The median percent RSD for the 23 target elements is 6.7 percent, almost the same as the Method 6010 QC solution percent RSD of 6.5 percent. Therefore, with the sole exception of silver, the added digestion procedure does not significantly change the precision of the analysis when the target elements are at concentrations of about 100 times the "Estimated IDL's" and are present in an interference-free matrix. The poor reproducibility of the silver determinations may be caused by the hydrochloric/nitric acid treatment during the Method 3050 digestion, or precipitation, or phototransformation of the silver ions in the analytical solution.

Method 3050/6010 Spiked Solids--

Two portions of the Method 3050/6010 solids were spiked prior to digestion with a blind spiking solution containing 19 of the 23 target elements. This was done so the resulting precision data could be used in conjunction with the precision data from the Method 6010 spiked bulk digests to calculate the method variances. These method variances result from the digestion procedure (Method 3050) and the ICP-AES measurement procedure (Method 6010).

The results for the determination of the 23 target elements in the Method 3050/6010 spiked solids are given in Table 10, and the percent RSD's for these spiked solids are summarized in Table 16. When Method 6010 and Method 3050 are applied in combination for the determination of the 23 elements in spiked solids, the apparent measurement precision decreases as indicated by the higher median percent RSD's (Table 16), when compared to the corresponding spiked bulk digest (Table 13) (with the exception of the fly ash spiked bulk digest). The median percent RSD's for the 7 solids, across the 23 elements, which were spiked prior to digestions to assure that the concentrations of the analytes were approximately 100 times greater than the instrument detection limit range from 10-19 percent (Table 16).

The median percent RSD for the fly ash spiked solid is 12 percent compared to 16 percent for the fly ash spiked bulk digest. It should be noted that the median percent RSD for the spiked solid of 12 percent includes the variance due to interlaboratory digestion differences. Therefore, this difference, although small, suggests that the presence of the high concentrations of V and Mo, is responsible for the increase in the median percent RSD or decrease in Method 6010 precision for this matrix in the spiked bulk digest.

The median percent RSD's for the 23 target elements, across the 7 spiked solids, are given in Table 14 in order of decreasing percent RSD (i.e., increasing precision of

TABLE 16. PERCENT RSD's FOR THE DETERMINATION OF THE 23 TARGET ELEMENTS IN THE SPIKED SOLIDS

ELEMENTS	HAZARDOUS WASTE 1	RIVER SEDIMENT	FLY ASH	ESTUARINE SEDIMENT	INDUSTRIAL SLUDGE	ELECTRO-PLATING SLUDGE	MINE TAILING
Al	17	24	20	22	14	18	26
Sb	27	56	25	62	28	40	58
As	13	26	16	22	20	20	22
Be	16	13	7.6	11	18	7.0	16
Cd	13	8.4	9.3	14	19	18	20
Ca	7.3	9.0	12	10	12	14	12
Cr	7.9	22	9.7	7.1	18	12	26
Co	18	22	12	9.2	18	13	18
Cu	12	14	10	9.7	19	9.4	12
Fe	14	19	44	16	18	14	18
Pb	15	6.4	9.6	11	20	19	5.8
Mg	5.9	8.4	17	9.0	16	10	10
Mn	14	9.0	11	10	16	18	9.4
Mo	19	31	24	18	18	43	20
Ni	13	20	9.7	10	20	15	17
Se	13	9.4	9.8	10	15	18	12
Ag	19	7.6	50	34	30	27	50
Tl	19	28	34	28	18	43	44
V	18	19	12	10	18	39	24
Zn	14	12	11	13	20	8.2	20
Ba	8.4	9.8	7.2	14	16	30	7.2
Na	14	40	32	9.4	20	15	12
K	19	17	18	18	22	5.7	16
MEDIAN PERCENT RSD	14	17	12	11	18	18	18

measurement by Method 3050/6010). Barium has the lowest median percent RSD of 9.8 percent and antimony has the highest of 40 percent. Silver and thallium also have high values of 30 percent and 28 percent respectively. In general, the precision of measurement for the 23 target elements by Method 3050/6010 for the spiked solids is poorer than that for the Method 6010 spiked bulk digests, more than likely caused by the addition of the Method 3050 digestion procedure.

Method 3050/6010 Unspiked Solids--

The results of the analysis of the Method 3050/6010 unspiked solids are found in Table 9. The median percent RSD's for the unspiked solids, across the 23 elements, range from 17-27 percent (Table 17). This poorer precision, when compared to the spiked solids, results because over 50 percent of the reported concentration values are less than 100 times the average of the instrumental detection limits. In other words, as the concentrations approach the instrumental detection limits, the precision decreases as indicated by the higher percent RSD's (Table 18). For 75 out of the 161 values (47 percent) given in Table 18, the percent RSD is greater than 20 percent. For 92 percent of those, the (mean concentration)/mean IDL) ratio is less than 100. In contrast, 86 out of the 161 values have percent RSD's less than or equal to 20 percent, and 79 percent of those have the (mean concentration/mean IDL) greater than or equal to 100 percent. Therefore, as the concentration of the analyte approaches the IDL, the precision of Method 3050/6010 dramatically decreases. For those elements that were present in the digests of the unspiked solids at concentrations 100 times greater than the IDL's, due to their occurrence in high concentrations in the unspiked solids, the precision is comparable to the precision for the spiked solid samples. Where examining the data in Table 9, caution should be exercised when 3 or more labs reported "ND" for a particular element. These values were excluded in the calculation of the mean concentration values, and therefore the percent RSD results from fewer data points.

ICP Analysis and Digestion Contributions to the Overall Method 3050/6010 Variance

The Method 6010 variance and the Method 3050 variance can be calculated from the data base on the Method 6010 spiked bulk digests in Table 7 and the Method 3050/6010 spiked solids in Table 10. For this consideration, the fly ash spiked bulk digests, containing the high-level Mo/V spike, was removed from the data base because of the biases from the high concentrations of V and Mo in this special Method 6010 spiked bulk digests.

TABLE 17. PERCENT RSD'S FOR THE DETERMINATION OF THE 23 TARGET ELEMENTS IN THE UNSPIKED SOLIDS

ELEMENTS	HAZARDOUS WASTE 1	RIVER SEDIMENT	FLY ASH	ESTUARINE SEDIMENT	INDUSTRIAL SLUDGE	ELECTRO-PLATING SLUDGE	MINE TAILING
Al	19	32	19	23	15	23	17
Sb	38	78	--	--	47	68	57
As	53	48	32	18	83	44	28
Be	31	27	27	35	42	70	41
Cd	37	17	57	52	17	22	59
Ca	9.0	13	10	11	10	17	8.6
Cr	11	19	28	22	12	12	90
Co	24	60	23	12	21	46	30
Cu	10	9.4	16	17	17	12	20
Fe	13	24	52	10	14	12	18
Pb	8.0	12	33	37	16	17	17
Mg	6.0	11	20	10	18	14	9.2
Mn	8.6	17	24	10	18	21	11
Mo	30	42	20	58	56	49	26
Ni	14	25	34	21	16	20	40
Se	42	61	--	30	43	74	77
Ag	41	43	47	1.4	38	54	60
Tl	31	30	--	--	38	45	120
V	21	72	15	17	28	35	47
Zn	14	12	20	8.6	12	9.2	20
Ba	7.4	11	4.3	14	24	38	8.8
Na	66	52	34	9.1	16	17	13
K	23	34	20	17	32	9.6	24
MEDIAN PERCENT RSD	21	27	23	17	18	22	26

TABLE 18. THE PRECISION (EXPRESSED AS PERCENT RSD) FOR EACH ELEMENT DETERMINED IN EACH OF THE SEVEN METHOD 3050/6010 UNSPIKED SOLIDS COMPARED TO THE RATIO OF THE MEAN CONCENTRATION OF EACH ELEMENT TO THE MEAN REPORTED IDLS

	River Sediment		Fly Ash		Estuarine Sediment		Mine Tailing		Hazardous Waste 1		Industrial Sludge		Electroplating Sludge	
	%RSD	Mean/IDL	%RSD	Mean/IDL	%RSD	Mean/IDL	%RSD	Mean/IDL	%RSD	Mean/IDL	%RSD	Mean/IDL	%RSD	Mean/IDL
Al	30	1000	20	3000	20	3000	20	3000	20	1000	10	3000	20	1000
Sb	90	70	60	2	60	2	100	3	70	2	80	2	60	30
As	70	10	30	30	100	4	30	100	60	4	90	4	50	7
Be	50	4	30	20	40	6	40	4	30	6	60	3	70	3
Cd	20	50	70	8	70	10	80	8	30	10	20	90	20	500
Ca	10	8000	9	1000	10	1000	8	3000	8	20000	10	20000	20	10000
Cr	20	7000	30	60	20	90	100	30	10	200	10	100	10	20000
Co	60	20	20	10	10	10	30	9	20	10	20	10	40	8
Cu	9	200	10	50	20	20	20	400	9	300	20	400	10	1000
Fe	20	50000	50	12000	9	16000	20	7000	10	10000	10	10000	10	20000
Pb	10	100	30	6	30	7	20	1000	7	40	20	3000	20	200
Mg	10	100	20	200	9	1800	9	3000	6	6000	20	500	10	400
Mn	10	3000	40	200	9	1000	10	400000	8	2000	20	3000	20	1000
Mo	70	20	20	30	100	4	30	70	60	7	90	5	70	20
Ni	40	40	30	30	20	20	40	20	10	20	10	200	20	400
Se	80	5	70	2	40	2	100	6	60	2	70	2	80	2
Ag	50	3	50	2	50	2	80	20	50	4	50	8	50	7
Tl	60	1	50	1	60	1	100	8	70	3	70	2	60	1
V	90	10	10	70	20	30	50	10	20	20	30	10	60	10
Zn	10	4000	20	100	8	200	20	800	10	400	10	3000	9	30000
Ba	10	100	4	2000	10	90	8	1000	7	400	20	10000	40	100
Na	50	200	30	40	9	1300	10	500	50	40	20	200	20	10000
K	30	20	20	60	20	100	20	300	20	20	30	10	9	70

An assumption that is made in the analysis of the data in this study is that the error distributions of concentration measurements are approximately log-normal. This implies that the mean and standard deviation are proportional to one another, and so the relative standard deviation is constant. Hence, to determine size and sources of variation, one may either investigate the relative standard deviations of measurements as has been done above, or one can perform a variance-components analysis on the log-transforms of the data. A detailed discussion of the variance components analysis of the log-transformed measurements is given in Appendix H. A summary of that analysis is given here.

If one lets Y_{ijk} represent the log-transform of the concentration of element k as measured by laboratory j in the analysis of Method 6010 spiked bulk digests i, then the variance across laboratories of this measurement may be represented by

$$Var(Y_{ijk})=\sigma_{Lik}^2+\sigma_{Eik}^2$$

where σ_{Lik}^2 represents the variance caused by differences between laboratories in application of Method 6010, and σ_{Eik}^2 represents within-laboratory analytical error variance. Similarly, let Y_{ijkm} represent the log-transformed measured concentration of element k in aliquot m from spiked Method 3050/6010 spiked solids i obtained by laboratory j. Then the variance across laboratories of Y_{ijkm} is

$$Var(Y_{ijkm})=\sigma_{Lik}^2+\sigma_{Bik}^2+\sigma_{Dik}^2+\sigma_{Eik}^2$$

where σ_{Bik}^2 is the variance that is caused by differences between laboratories in applying Method 3050 digestion, σ_{Dik}^2 is the variance between aliquots within laboratories applying Method 3050 digestion, and σ_{Lik}^2 and σ_{Eik}^2 are as defined above. The estimator

$$s_{1ik}^2=\Sigma(Y_{ijk}-\overline{Y}_{ik})^2/(n-1)$$

where n is the number of laboratories providing measurements, has expected value $(\sigma_{Lik}^2+\sigma_{Eik}^2)$. If $\sigma_{Lik}^2=\sigma_{Lk}^2$ and $\sigma_{Eik}^2=\sigma_{Ek}^2$ for all performance evaluation materials i (i.e., the variances are homogeneous across the evaluation materials), the the estimators s_{1ik}^2 can be pooled to obtain the unbiased estimator s_{2k}^2 of $(\sigma_{Lk}^2+\sigma_{Ek}^2)$. This variance $(\sigma_{Lk}^2+\sigma_{Ek}^2)$ represents the "total ICP (Method 6010) variance" for element k. Similary, if $\sigma_{Bik}^2=\sigma_{Bk}^2$ and $\sigma_{Dik}^2=\sigma_{Dk}^2$, for all performance evaluations i, the estimators

$$s_{3ik}^2=\Sigma_j(Y_{ijk1}-Y_{ijk2})^2/2n$$

and

$$s_{4ij}^2 = 2\Sigma_j(Y_{ijk} - \overline{Y}_{ik})^2/(n-1)$$

may be pooled over performance evaluations to obtain unbiased estimators s_{5k}^2 of the "total within-lab Variance ($\sigma_{Dk}^2 + \sigma_{Ek}^2$) and s_{6k}^2 of ($2\sigma_{Lk}^2 + 2\sigma_{Bk}^2 + \sigma_{Dk}^2 + \sigma_{Ek}^2$). Now ($s_{5k}^2 + s_{6k}^2$)/2 is an unbiased estimator of the "total variance" ($\sigma_{Lk}^2 + \sigma_{Bk}^2 + \sigma_{Dk}^2 + \sigma_{Ek}^2$) of a measurement of element k using the Method 3050/6010 procedure ($s_{6k}^2 - s_{5k}^2$)/2 is an unbiased estimator of the "total between-lab Variance" ($\sigma_{Lk}^2 + \sigma_{Bk}^2$); and ($s_{5k}^2 + s_{6k}^2 - 2s_{2k}^2$)/2 is an unbiased estimator of the "total digestion variance" ($\sigma_{Bk}^2 + \sigma_{Dk}^2$).

The pooled variance estimates were calculated after removal of outliers and ND's from the data (see Tables 7 and 10). The above described linear combinations of the pooled variance estimates are given in Table 19. The median total ICP variance estimate and the median total digestion variance estimate are approximately equal and no clear pattern of dominance between the two variances is discernible. This indicates that the Method 3050 digestion and Method 6010 make about equal contributions to total variance when concentrations are considerably above instrument detection limits. Also, as might be expected, Table 19 indicates that between-laboratory variability is considerably greater than within-laboratory variability. Table 20 presents total ICP variance and total digestion variance as percentages of total variance.

ACCURACY

Accuracy determinations require a comparison of a measured value to a "true" value. The Method 6010 and Method 3050/6010 QC solutions were carefully prepared from high-purity standard solutions. Thus, the reported concentration values for the 23 target elements can be compared to the "prepared" values to yield an estimate of accuracy for the interference-free QC solutions in which the concentrations of all elements were approximately 100 times the "Estimated 6010 IDL's." The Method 6010 accuracy can be estimated from the results on the Method 6010 QC solutions given in Table 8, and, similarly, the Method 3050/6010 accuracy can be estimated from the Method 3050/6010 QC solutions data given in Table 11.

One of the Method 3050/6010 solids, the mine tailing material (Table 1), is a CLP solid reference material for which the "true" value concentrations of many of the target elements were previously determined by a referee analysis by using the CLP Method (ICP-AES), which is similar to Method 3050/6010. Therefore, the results obtained in this study can be compared with the CLP "true" values. In addition, the accuracy of Method 6010 is discussed in terms of spike recovery, and the

TABLE 19. POOLED VARIANCE ESTIMATES OF VARIANCE COMPONENTS BASED ON METHOD 6010 SPIKED BULK DIGESTS AND METHOD 3050/6010 SPIKED SOLIDS DATA

	ESTIMATES				
Elements	Total Digest Variance A	Total ICP Variance B	Total Between-Lab. Var. C	Total Within-Lab. Var. D	Total Variance E
Al	0.0043	0.0030	0.0065	0.0008	0.0073
Cd	0.0039	0.0014	0.0042	0.0011	0.0053
Ca	0.0012	0.0012	0.0019	0.0005	0.0024
Co	0.0036	0.0023	0.0052	0.0007	0.0059
Cu	0.0023	0.0014	0.0031	0.0006	0.0037
Fe	0.0100	0.0012	0.0099	0.0013	0.0112
Pb	0.0013	0.0025	0.0034	0.0004	0.0038
Mg	0.0000[a]	0.0031	0.0019	0.0004	0.0024
Mn	0.0011	0.0023	0.0026	0.0008	0.0034
Mo	0.0000[a]	0.0159	0.0115	0.0008	0.0147
Ni	0.0041	0.0015	0.0044	0.0012	0.0056
Se	0.0004	0.0033	0.0033	0.0004	0.0037
Tl	0.0077	0.0130	0.0128	0.0079	0.0207
Zn	0.0009	0.0023	0.0031	0.0011	0.0042
Ba	0.0031	0.0018	0.0025	0.0024	0.0049
K	0.0043	0.0012	0.0044	0.0012	0.0055
Be[1]	0.0027	0.0009	0.0023	0.0013	0.0036
V[1]	0.0079	0.0025	0.0079	0.0025	0.0104
As[2]	0.0053	0.0029	0.0073	0.0008	0.0082
Sb[2]	0.0439	0.0014	0.0426	0.0027	0.0453
Cr[2]	0.0029	0.0010	0.0036	0.0003	0.0039
Na[2]	0.0068	0.0023	0.0087	0.0004	0.0091
Ag[3]	0.0000[a]	0.0287	0.0191	0.0059	0.0250
Median[3]	0.0027	0.0023	0.0038	0.0008	0.0051

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[1] Pooled variance in Column B is based on six Method 6010 spiked bulk digests (excluding Fly Ash) whose set of variance estimates satisfy the homogeneity test.

[2] Variance estimates in Column B are medians of the 7 sample s_{lik}^2 values because of the heterogeneity of the variances for these elements.

[3] Medians are over variance estimates for first 17 listed elements.

[a] Estimate set to zero because the difference used in calculating the variance estimate gave a negative value.

TABLE 20. ESTIMATED PERCENTAGE CONTRIBUTIONS OF METHOD 6010 ICP VARIANCE AND METHOD 3050 DIGESTION VARIANCE TO TOTAL VARIANCE

Elements	6010 ICP	3050 Digestion
Al	41	59
Cd	26	74
Ca	50	50
Co	39	61
Cu	38	62
Fe	11	89
Pb	66	34
Mg	100	0[a]
Mn	68	32
Mo	100	0[a]
Ni	27	73
Se	89	11
Tl	63	37
Zn	55	45
Ba	37	63
K	22	76
Be[1]	25	75
V[1]	24	76
Sb[2]	3	97
As[2]	35	65
Cr[2]	26	74
Na[2]	25	75
Ag[3]	100	0[a]
Median[3]:	46	55

[1,2,3,a] See correspondingly denoted footnotes in Table 19.

Method 6010 spiked bulk digests results are compared to atomic absorption spectroscopy results. Simultaneous-ICP results for the Method 6010 spiked bulk digests are also compared to sequential ICP results in this section.

Interference-free Method 6010 and Method 3050/6010 QC Solutions

Table 21 gives the value of the arithmetic mean of the elemental concentration reported by the participating laboratories that is divided by the true values of the four blind QC solutions. Examination of this table indicates that Method 6010 and Method 3050/6010 perform very well in terms of the accurate determination of 22 of the 23 elements in that the results are within 7 percent of the "known" or "prepared" values. The ICP determination for silver with and without digestion yields significantly low values that may be indicative of the amount of silver that actually reached the ICP plasma for quantitation. The low silver results may be caused by precipitation of AgCl in the presence of chloride, which is introduced in the Method 3050 digestion procedure as HCl or by some phototransformation process that reduces the amount of silver in solution. In general, silver is consistently the element with the lowest precision (highest percent RSD) [see Tables 12 and 14]. Moreover, for interference-free matrices and at element concentrations near 100 times the IDL, Method 6010 and Method 3050/6010 very accurately measure 22 of the 23 target elements (silver excluded).

Mine Tailing Solid (unspiked)

This solid is a reference material used in the CLP as a solid laboratory control sample to check the accuracy of the CLP digestion and ICP-AES analysis procedures. Overall, the CLP procedure is very similar to Method 3050/6010. The Method 3050/6010 results for the analysis of the unspiked mine tailing solid duplicates are given in Table 22 along with the "true" values. In Duplicate No. 1, Cu, Se, and Tl values are outside the EPA-CLP control limits, and for Duplicate No. 2, Se and Tl are outside. Copper is low by only 5 mg/kg or 2 percent, but Se and Tl appear to be high in both samples. However, the average LOD for Se and Tl are 10 mg/kg and 9 mg/kg, respectively (Table 5B). Therefore, the upper control limit of 11 mg/kg for Se in the mine tailing is at the average Method 6010 LOD and the upper control limit of 26 mg/kg for Tl is at three times the average Method 6010 LOD or approximately the average Method 6010 LOQ. Six of the laboratories reported Se as not detected for Duplicate No. 1 and five reported it as not detected for Duplicate No. 2. For thallium, four laboratories reported it as not detected in both duplicate samples. Therefore, the high mean values reported in Table 22 result

TABLE 21. ACCURACY ESTIMATES FROM ANALYTICAL RESULTS FROM METHOD 6010 AND METHOD 3050/6010 QC SOLUTIONS

Element	Method 6010 QC Solutions Concentration Mean/Target	Method 3050/6010 QC Solutions Concentration Mean/Target
Al	1.00	0.98
Sb	1.00	1.00
As	0.99	0.97
Be	1.02	0.98
Cd	0.98	1.03
Ca	1.02	0.99
Cr	1.02	0.99
Co	0.96	0.96
Cu	0.97	0.96
Fe	1.00	0.99
Pb	0.98	0.95
Mg	0.98	0.95
Mn	1.02	0.96
Mo	0.99	0.96
Ni	1.00	0.98
Se	1.04	0.97
Ag	0.82*	0.53*
Tl	1.02	0.93
V	0.95	0.96
Zn	0.95	0.93
Ba	1.00	0.96
Na	0.96	0.97
K	0.96	0.95
mean	0.99±0.03	0.97±0.03

* Underlined values indicate outlier values and are not included in the calculation of the means.

TABLE 22. RESULTS FOR THE METHOD 3050/6010 ANALYSIS OF THE UNSPIKED MINE TAILING SAMPLE COMPARED TO THE EPA CLP CONTROL LIMITS*

DUPLICATE No.1

ELEMENT	MEAN	STD DEV	RSD (%)	CLP CONTROL LIMITS TRUE	LOWER	UPPER	MEAN/TRUE	WITHIN LIMITS
Al	13900	1580	11	15200	7500	22900	0.91	YES
Sb	12	19	158	<20	0	44		YES
As	618	161	26	680	380	980	0.91	YES
Be	0.5	0.2	49	<1	0	1.6		YES
Cd	1.7	1.4	83	<1	0	7.8		YES
Ca	9850	718	7	10520	7850	13200	0.94	YES
Cr	12	12	104	17	0	46	0.71	YES
Co	7.2	2.1	29	6.9	0	19	1.05	YES
Cu	215	63	30	265	220	310	0.81	NO
Fe	10300	1580	15	11200	5910	16500	0.92	YES
Pb	5660	1050	19	5830	4310	7340	0.97	YES
Mg	14200	1040	7	14730	10910	18560	0.96	YES
Mn	92800	926	1	91735	68600	114900	1.01	YES
Mo[a]	56	16	29					
Ni	21	8.9	43	22	5.0	39	0.93	YES
Se[b]	43	51	117	<1	0	11		NO
Ag	8.0	6.8	85	<2	0	26		NO
Tl[c]	73	107	146	3.8	0	9.1	19.23	NO
V	13	7.2	54	19	0	46	0.72	YES
Zn	362	71	19	425	317	535	0.85	YES
Ba	397	43	11	430	360	510	0.92	YES
Na	3390	374	11					
K	8130	2620	32	8150	4540	11770	1.00	YES

(continued)

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* Concentrations in mg/kg.

[a] Mo is not a CLP element.

[b] The average LOD for Se is 10 mg/kg.

[c] The average LOD for Tl is 9 mg/kg.

TABLE 22. (concluded)

DUPLICATE No.2

ELEMENT	MEAN	STD DEV	RSD (%)	CLP TRUE	CONTROL LIMITS LOWER	CONTROL LIMITS UPPER	MEAN/TRUE	WITHIN LIMITS
Al	14300	3170	22	15200	7500	22900	0.94	YES
Sb	5.8	4.2	74	<20	0	44		YES
As	636	185	29	680	380	980	0.94	YES
Be	0.5	0.2	39	<1	0	1.6		YES
Cd	1.6	1.4	87	<1	0	7.8		YES
Ca	9670	962	10	10520	7850	13200	0.92	YES
Cr	15	15	100	17	0	46	0.89	YES
Co	7.8	2.6	33	6.9	0	19	1.13	YES
Cu	235	25	11	265	220	310	0.89	YES
Fe	9810	2070	21	11200	5910	16500	0.88	YES
Pb	5550	846	15	5830	4310	7340	0.95	YES
Mg	14300	1540	11	14730	10910	18560	0.97	YES
Mn	92300	11000	12	91735	68600	114900	1.01	YES
Mo[a]	55	14	26					
Ni	21	8	37	22	5.0	39	0.93	YES
Se[b]	43	49	112	<1	0	11		NO
Ag	7.5	6.3	84	<2	0	26		YES
Tl[c]	74	105	141	3.8	0	9.1	19.54	NO
V	13	8.1	62	19	0	46	0.71	YES
Zn	358	71	20	425	317	535	0.84	YES
Ba	414	27	7	430	360	510	0.96	YES
Na	3340	477	14					
K	7350	1112	15	8150	4540	11770	0.90	YES

from the laboratories that reported detectable Se and Tl values, which does not reflect the fact that many reported them as not detected (see Table 10). Overall, the Method 3050/6010 analysis of the mine tailing solids gave very accurate results. The Mo and Na CLP "True" Values do not exist so no comparison for those two elements is possible.

Spike Recovery and Accuracy - Method 3050/6010

The participating laboratories prepared duplicate samples of the Method 3050/6010 spiked solids. Four-gram amounts of these solids were spiked with 2 mL of the blind spiking solutions. The composition of the spiking solutions was known by the coordinating laboratory so that the spike recovery data could be derived from the reported data.

The spike recoveries were calculated from the data given in Tables 9 and 10. The spike recovery results from the nine participating laboratories are summarized in Table 23 for the 7 spiked solids. The median spike recovery for each element is given in Table 24.

The median percent recoveries for 12 of the 19 elements are shown to be equal to or greater than 85 percent (Table 24), which is very good. These 12 elements are Be, Cd, Cr, Cu, Pb, Mn, Mo, Ni, Se, V, Zn, and Ba. Good spike recoveries suggest that good accuracy can also be expected for these 12 elements.

The three elements, As, Co, and Tl, have median spike recoveries between 73 and 84 percent. Four elements have low spike recoveries. These are Ag (68 percent), Na (45 percent), K (48 percent), and Sb (51 percent). Two of these four elements, silver and antimony, have the highest percent RSD's in the Method 6010 and Method 3050/6010 results. As discussed earlier, Ag may have precipitated as AgCl. Antimony can precipitate as oxides and oxo chlorides in the nitric hydrochloric acid matrix that results in the Method 3050 digestion (4,5). In several of the spiked solid digests, the spike levels of K and Na were up to 100 times less than the endogenous levels, and this results in a highly uncertain calculation of the spike recovery. Moreover, the CLP Inorganic Protocol does not consider spike recovery data when the spike level is less than one-fourth of the endogenous level.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) Versus Atomic Absorption Spectroscopy (AAS)

The accuracy of the ICP Method 6010 can be further estimated by comparing the average concentrations for the Method 6010 spiked bulk digests to the corresponding concentrations determined by AAS by one of the participating

TABLE 23. MEAN PERCENT RECOVERIES OF THE ELEMENTS IN THE METHOD 3050/6010 SPIKED SOLIDS

	Sample						
Element	Hazardous Waste 1	River Sediment	Estuarine Sediment	Fly Ash	Mine Tailing	Electro-Plating Sludge	Industrial Sludge
Al**	-	-	-	-			
Sb	51^a	67^b	24^a	57^a	8^a	62^a	34^a
As	82^a	76^a	84^a	95^a	99^b	90^a	81^a
Be	89^a	87^a	95^a	94^a	83^a	84^a	85^a
Cd	81^a	85^a	97^a	92^a	88^a	75^b	90^a
Ca**	-	-	-	-	-	-	-
Cr	87^b	X^e	95^a	103^a	65^a	X^e	86^b
Co	87^a	78^a	84^a	94^a	79^a	78^a	81^a
Cu	99^b	94^b	93^a	94^a	82^b	78^d	85^c
Fe**	-	-	-	-	-	-	-
Pb	67^a	84^b	92^a	96^a	X^d	121^b	^{d}
Mg**	-	-	-	-	-	-	-
Mn	109^c	94^d	98^b	97^a	X^e	53^c	91^d
Mo	88^a	89^a	90^a	91^a	72^b	82^b	72^a
Ni	86^a	90^a	97^a	100^a	84^a	80^c	95^b
Se	87^a	85^a	92^a	91^a	86^a	93^a	83^a
Ag	84^a	68^a	67^a	87^a	61^a	34^a	76^a
Tl	75^a	72^a	80^a	66^a	62^b	X^a	77^a
V	86^a	78^a	92^a	92^b	77^a	52^a	85^a
Zn	93^b	32^d	100^b	100^b	31^b	X^e	122^d
Ba	98^b	93^a	97^a	87^d	98^c	-6^b	X^e
Na	44^a	46^b	65^c	43^a	47^b	X^d	42^b
K	47^a	52^a	58^b	48^b	-1^c	42^b	44^a

* X indicates values much <0 or >100.

** Not spiked.

a. (Mean Unspiked Sample Result)/(Spike Concentration) < 1

b. $1 \leq$ (Mean Unspiked Sample Result)/(Spike Concentration) ≤ 4

c. $4 \leq$ (Mean Unspiked Sample Result)/(Spike Concentration) ≤ 10

d. $10 <$ (Mean Unspiked Sample Result)/(Spike Concentration) ≤ 100

e. (Mean Unspiked Sample Result)/(Spike Concentration) > 100

TABLE 24. MEDIAN PERCENT SPIKE RECOVERIES OF ELEMENTS IN THE METHOD 3050/6010 SPIKED SOLIDS

Element	Median % Recovery
Al*	--
Sb	51
As	84
Be	87
Cd	88
Ca*	--
Cr	87
Co	81
Cu	93
Fe*	--
Pb	92
Mg*	--
Mn	95
Mo	88
Ni	90
Se	87
Ag	68
Tl	73
V	85
Zn	97
Ba	97
Na	45
K	48

*Not Spiked.

laboratories. Although bias may be present, quantitative agreement of absolute elemental concentrations by two independent measurement methods does tend to corroborate the results. Therefore, agreement between the two instrumental methods will be assumed to be a confirmation of accuracy.

Comparative data for the Method 6010 spiked bulk digests analyzed by ICP-AES and AAS are given in Table 25. The ratio of the average ICP-AES value to the AAS value is also given. A null hypothesis approach that is based on the mean and the corresponding standard deviation was used to determine if the ICP-AES and AAS values are significantly different at the 95 percent confidence level (6). The result is shown in the table under the column headed "Sig. Dif." The results in Table 25 indicate that only 2 out of 184 elemental measurements by the 2 methods are significantly different. In some cases where the ICP-AES/AAS ratios are very different (less than 0.75 or greater than 1.25), the standard deviations in the ICP measurements are very high, and, therefore, the differences in the means are not significant.

In Table 25, an ICP-AES/AAS ratio greater than 1.25 is designated by a plus "+" sign, and a ratio less than 0.75 is indicated by a minus "-" sign. Of the 39 values that are marked, 29 are on the positive side; that is, the ICP-AES Method 6010 overestimated the result compared to the AAS procedure. Thallium accounts for eight of the 29 high values, and it is high in the 7 Method 6010 spiked bulk digests and the Method 6010 QC solutions by an average ICP-AES/AAS ratio of 1.81. The fly ash Method 6010 spiked bulk digests that contained 1,000,000 ppb (0.1 percent) V and Mo has 11 of the 39 results in which the ICP-AES/AAS ratio differs from 1.0 by more than 0.25. For the fly ash spiked bulk digest, the Sb, As, Be, Ca, Cu, Tl, V, and Na values are high, and the Ni, Se and Ag values are low. Again, it is apparent that the fly ash matrix with high levels of added V and Mo adversely affects the determination of many of the 23 target elements. Overall, the agreement between ICP-AES and AAS is excellent.

Simultaneous ICP Versus Sequential ICP

Two of the 9 participating laboratories used simultaneous ICP instruments, and the other 7 used sequential ICP instruments for this study. The Method 6010 spiked bulk digests are not subject to the uncertainties introduced by the Method 3050 digestion procedure, and thus data from the Method 6010 spiked bulk digests are used to compare sequential and simultaneous ICP-AES results.

The average analytical values from sequential and simultaneous instrumental analysis of the 23 elements in the

TABLE 25. COMPARISON OF ICP-AES AND AAS DATA FOR METHOD 6010 SPIKED BULK DIGESTS

	HAZARDOUS WASTE 1				RIVER SEDIMENT				FLY ASH				ESTUARINE SEDIMENT			
	CONC. (ug/L)				CONC. (ug/L)				CONC. (ug/L)				CONC. (ug/L)			
ELEMENTS	ICP MEAN	AA	ICP/AA	SIG. DIF. *	ICP MEAN	AA	ICP/AA	SIG. DIF. *	ICP MEAN	AA	ICP/AA	SIG. DIF. *	ICP MEAN	AA	ICP/AA	SIG. DIF. *
Al	127000	97400	1.30^{+}	NO	110000	83100	1.32^{+}	NO	330000	317000	1.04	NO	346000	368000	0.94	NO
Sb	4930	4400	1.12	NO	11200	4200	2.67^{+}	NO	7880	3500	2.25^{+}	NO	5030	4000	1.26^{+}	NO
As	4900	5300	0.92	NO	6180	6400	0.97	NO	21000	7700	2.73^{+}	NO	6800	5600	1.21	NO
Be	928	701	1.32^{+}	NO	945	725	1.30^{+}	NO	3960	859	4.61^{+}	NO	951	780	1.22	NO
Cd	912	1070	0.85	NO	1130	1190	0.95	NO	955	960	0.99	NO	911	1030	0.88	NO
Ca	1380000	1420000	0.97	NO	519000	488000	1.06	NO	102000	42100	2.42^{+}	NO	76300	33300	2.29^{+}	YES
Cr	2910	3540	0.82	NO	541000	544000	0.99	NO	1820	1960	0.93	NO	1720	2150	0.80	NO
Co	1050	1240	0.85	NO	1190	1260	0.94	NO	1050	1280	0.82	NO	1080	1210	0.89	NO
Cu	4000	4190	0.95	NO	2780	2950	0.94	NO	2360	1590	1.48^{+}	NO	1120	1290	0.87	NO
Fe	358000	338000	1.06	NO	1540000	1640000	0.94	NO	602000	591000	1.02	NO	507000	501000	1.01	NO
Pb	8720	9400	0.93	NO	15600	18300	0.85	NO	5440	4870	1.12	NO	5390	5390	1.00	NO
Mg	479000	552000	0.87	NO	121000	136000	0.89	NO	14900	13500	1.10	NO	151000	133000	1.14	NO
Mn	7580	8370	0.91	NO	13100	14500	0.90	NO	1650	1770	0.93	NO	5120	5760	0.89	NO
Mo	940	963	0.98	NO	1040	1250	0.83	NO	891000	851000	1.05	NO	704	1010	0.70^{-}	NO
Ni	1360	1580	0.86	NO	1510	1870	0.81	NO	1260	1720	0.73^{-}	NO	1420	1540	0.92	NO
Se	7380	8900	0.83	NO	6960	8700	0.80	NO	6270	8800	0.71^{-}	NO	7530	8700	0.87	NO
Ag	812	1050	0.77	NO	932	1070	0.87	NO	578	995	0.58^{+}	NO	779	1030	0.76	NO
Tl	4450	2760	1.61^{+}	NO	4770	2770	1.72^{+}	NO	5900	2550	2.31^{-}	NO	3670	2710	1.35^{+}	NO
V	1240	1520	0.82	NO	828	1410	0.59^{-}	NO	630000	101000	6.24^{+}	NO	1770	2000	0.89	NO
Zn	4330	4700	0.92	NO	30300	33000	0.92	NO	1900	2310	0.82	NO	2960	3330	0.89	NO
Ba	4360	5830	0.75^{-}	NO	1850	2500	0.74^{-}	NO	13300	13200	1.01	NO	1690	1710	0.99	NO
Na	15600	1500	10.40	NO	37300	29400	1.27^{+}	NO	20000	14900	1.34^{+}	NO	203000	209000	0.97	NO
K	23800	27500	0.87	NO	19200	21000	0.91	NO	46400	47500	0.98	NO	75300	93000	0.81	NO

* Result of a null hypothesis approach used to indicate whether the ICP and AA results are significantly different.

+ ICP/AA ratio greater than 1.25.

- ICP/AA ratio less than or equal to 0.75.

(continued)

TABLE 25. (concluded)

ELEMENTS	INDUSTRIAL SLUDGE CONC. (ug/L) ICP MEAN	AA	ICP/AA	SIG. DIF. *	ELECTROPLATING SLUDGE CONC. (ug/L) ICP MEAN	AA	ICP/AA	SIG. DIF. *	MINE TAILING CONC. (ug/L) ICP MEAN	AA	ICP/AA	SIG. DIF. *
Al	225000	240000	0.94	NO	127000	116000	1.09	NO	331000	336000	0.99	NO
Sb	4820	4300	1.12	NO	5870	4300	1.37^{+}	NO	4900	4100	1.20	NO
As	4810	5500	0.87	NO	5380	6000	0.90	NO	16500	19000	0.87	NO
Be	901	756	1.19	NO	892	838	1.06	NO	1790	400	4.48^{+}	NO
Cd	1200	1430	0.84	NO	135000	3190	42.32^{+}	NO	901	1009	0.89	NO
Ca	1250000	1220000	1.02	NO	835000	983000	0.85	NO	216000	110000	1.96^{+}	YES
Cr	1840	2440	0.75^{-}	NO	135000	165000	0.82	NO	1400	1400	1.00	NO
Co	1060	1190	0.89	NO	19800	1190	16.64^{+}	NO	1020	1150	0.89	NO
Cu	6090	6440	0.95	NO	15600	16100	0.97	NO	5310	6280	0.85	NO
Fe	300000	297000	1.01	NO	645000	588400	1.10	NO	248000	238000	1.04	NO
Pb	280000	275000	1.02	NO	24600	25800	0.95	NO	96900	119000	0.81	NO
Mg	38400	47400	0.81	NO	34800	41200	0.84	NO	297000	302000	0.98	NO
Mn	12700	15400	0.82	NO	5630	6220	0.91	NO	1760000	1730000	1.02	NO
Mo	749	1040	0.72^{-}	NO	1200	1240	0.97	NO	2120	2280	0.93	NO
Ni	3770	4270	0.88	NO	8600	10500	0.82	NO	1380	1460	0.95	NO
Se	7500	8700	0.86	NO	8070	8600	0.94	NO	7660	8400	0.91	NO
Ag	818	1080	0.76	NO	882	278	3.17^{+}	NO	990	1020	0.97	NO
Tl	4530	2750	1.65^{+}	NO	4410	2850	1.55^{+}	NO	6970	2790	2.50^{+}	NO
V	1080	1360	0.79	NO	1070	1540	0.69^{-}	NO	1180	1520	0.78	NO
Zn	25700	29900	0.86	NO	260000	263000	0.99	NO	8920	10100	0.88	NO
Ba	165000	172000	0.96	NO	1640	2840	0.58^{-}	NO	9170	10100	0.91	NO
Na	43200	45800	0.94	NO	1380000	1450000	0.95	NO	76400	85500	0.89	NO
K	17400	19500	0.89	NO	50900	62300	0.82	NO	175000	169000	1.04	NO

Method 6010 spiked bulk digests are given in Table 26. The column labeled "Ratio %" is the value ofthe sequential mean data divided by the simultaneous mean data given as a percentage. The last column, labeled "Sig. Dif.", indicates whether the difference in the two means is significantly different from zero. This null hypothesis determination is based on comparison of the means and the corresponding standard deviations at the 95 percent confidence level (6). The results in Table 26 indicate that only 7 out of 184 elemental measurements made by using 2 different ICP-AES instrument types are significantly different. By contrast, a statistical comparison of two randomly selected sets of data from two sequential instruments with the sets of data from the remaining five sequential instruments also yields seven significantly different analytical values. This comparison indicates that the differences between the sequential and simultaneous instrument results are due to random variations in the data; in other words, the data from the two types of instruments are indistinguishable.

MSA Versus Non-MSA Results

The Method 6010 task directive required that MSA be performed whenever the ICP-AES results for an element for a four-fold dilution of the sample solution was a factor of 10 above the reported IDL and whenever multiplication of the diluted concentration by four did not produce a concentration within ± 10 percent of the undiluted concentration. The MSA data in Tables 7 through 11 are flagged with an asterisk.

The participating laboratories performed 725 MSA's out of a total 7,475 analyses (less than 10 percent) as reported in Tables 7 through 11. In most of these cases, only one or two MSA's were performed; that is, only one or two laboratories out of nine had to perform the MSA on a given element in a given matrix. A comparison of MSA results for such cases (when one or two MSA's for an element are reported) is not statistically meaningful. Those performance evaluation materials and elements for which three or more MSA's were reported are given in Table 27. Table 27 compares the mean MSA results and non-MSA results for these cases. This table shows that more MSA's were performed for the fly ash Method 6010 spiked bulk digest than for any other Method 6010 spiked bulk digests. (This sample was spiked with high concentrations of Mo and V and has the highest percent RSD's of all the Method 6010 solutions.)

Statistical examination of the data in Table 27 shows that the results obtained by the application of the MSA were equivalent to non-MSA results in 45 out of 51 cases (88 percent) at the 95 percent confidence level (6). There are 14

TABLE 26. COMPARISON OF DATA OBTAINED FROM THE ANALYSIS OF THE METHOD 6010 SPIKED BULK DIGEST BY USING SIMULTANEOUS AND SEQUENTIAL ICP-AES.

	HAZARDOUS WASTE 1				RIVER SEDIMENT				FLY ASH			
	MEAN CONC. (ug/L)				MEAN CONC. (ug/L)				MEAN CONC. (ug/L)			
ELEMENTS	SEQ.	SIMUL.	RATIO (%)	SIG. DIF.*	SEQ.	SIMUL.	RATIO (%)	SIG. DIF.*	SEQ.	SIMUL.	RATIO (%)	SIG. DIF.*
Al	125514	119500	105	N	109586	97400	113	N	333100	311000	107	N
Sb	4919	4705	105	N	11984	4920	244	N	8416	3795	222	N
As	5014	4695	107	N	6115	6530	94	N	21599	12050	179	N
Be	883	970	91	N	900	990	91	N	4218	1512	279	N
Cd	928	932	100	N	1138	1125	101	N	953	963	99	N
Ca	1364714	1455000	94	N	506471	548000	92	N	99571	79000	126	N
Cr	2988	2955	101	N	545143	530000	103	N	2000	1270	157	N
Co	1070	1075	100	N	1223	1130	108	N	1220	557	219	Y
Cu	4031	3980	101	N	2824	2730	103	N	1726	4215	41	N
Fe	351800	371500	95	N	1740286	897600	194	Y	592114	631000	94	N
Pb	8631	9375	92	N	15269	18000	85	N	5234	5870	89	N
Mg	488086	482000	101	N	121714	128000	95	N	14500	15450	94	N
Mn	7645	7735	99	N	13051	13900	94	N	1581	1945	81	N
Mo	918	1030	89	N	1071	1043	103	N	854543	998000	86	N
Ni	1374	1435	96	N	1514	1690	90	N	1247	1530	81	N
Se	7611	7350	104	N	7060	7500	94	N	7014	4930	142	N
Ag	819	908	90	N	929	1012	92	N	769	117	657	N
Tl	4205	4450	94	N	4553	4550	100	N	6412	2425	264	N
V	1277	1260	101	N	884	925	96	N	720437	505001	143	N
Zn	4378	4330	101	N	31881	26250	121	Y	2083	1460	143	N
Ba	4534	4475	101	N	1944	1902	102	N	13414	12900	104	N
Na	13814	15500	89	N	39271	26500	148	N	20779	14800	140	N
K	25843	26550	97	N	19900	17700	112	Y	46724	46000	102	N

*Sig.Dif., Results of a null hypothesis approach used to indicate whether the concentration results from sequential and simultaneous instruments are significantly different at the 95% confidence level.

(continued)

TABLE 26. (continued)

ELEMENTS	ESTUARINE SEDIMENT				INDUSTRIAL SLUDGE				ELECTROPLATING SLUDGE			
	MEAN CONC. (ug/L) SEQ.	MEAN CONC. (ug/L) SIMUL.	RATIO (%)	SIG. DIF.*	MEAN CONC. (ug/L) SEQ.	MEAN CONC. (ug/L) SIMUL.	RATIO (%)	SIG. DIF.*	MEAN CONC. (ug/L) SEQ.	MEAN CONC. (ug/L) SIMUL.	RATIO (%)	SIG. DIF.*
Al	344643	361000	95	N	224486	234500	96	N	128543	117500	109	N
Sb	4961	4740	105	N	4784	4675	102	N	5890	5000	118	N
As	7180	4875	147	N	5181	3850	135	N	5413	5585	97	N
Be	914	995	92	N	875	919	95	N	877	919	95	N
Cd	928	913	102	N	1230	1225	100	N	153930	2865	5373	N
Ca	70129	76600	92	N	1227429	1310000	94	N	806634	1009500	80	N
Cr	1803	1650	109	N	1933	1830	106	N	135134	150000	90	N
Co	1089	1110	98	N	1081	1070	101	N	22437	1105	2030	N
Cu	1121	1200	93	N	6146	6055	102	N	15949	14550	110	N
Fe	498943	533500	94	N	295771	315000	94	N	638086	642000	99	N
Pb	5386	5395	100	N	279857	276500	101	N	24639	24900	99	N
Mg	150086	144500	104	N	41414	32350	128	N	36499	31950	114	N
Mn	5125	5420	95	N	14571	7485	195	Y	5596	6060	92	N
Mo	862	306	281	N	882	427	206	N	1247	1060	118	N
Ni	1456	1365	107	N	3949	3410	116	N	8619	9490	91	N
Se	7647	7705	99	N	7629	7670	99	N	8008	8545	94	N
Ag	782	896	87	N	840	874	96	N	787	913	86	N
Tl	3174	4945	64	N	4634	3265	142	N	3919	5340	73	N
V	1811	1760	103	N	1110	1110	100	N	1117	1140	98	N
Zn	2931	3265	90	N	28380	18500	153	Y	260829	260000	100	N
Ba	1706	1655	103	N	166629	162500	103	N	1789	1715	104	N
Na	206486	193500	107	N	48071	27300	176	Y	1401714	1335000	105	N
K	84843	50700	167	Y	18271	15450	118	N	52704	50300	105	N

(continued)

TABLE 26. (concluded)

ELEMENTS	MINE TAILINGS MEAN CONC. (ug/L) SEQ.	MINE TAILINGS MEAN CONC. (ug/L) SIMUL.	MINE TAILINGS RATIO (%)	MINE TAILINGS SIG. DIF.*	METHOD 3050 QC SAMPLES MEAN CONC. (ug/L) SEQ.	METHOD 3050 QC SAMPLES MEAN CONC. (ug/L) SIMUL.	METHOD 3050 QC SAMPLES RATIO (%)	METHOD 3050 QC SAMPLES SIG. DIF.*
Al	372471	188000	198	N	14870	14550	102	N
Sb	4801	4840	99	N	14317	16350	88	N
As	16657	17350	96	N	15026	15400	98	N
Be	1828	972	188	N	3706	22580	16	N
Cd	919	890	103	N	3555	3870	92	N
Ca	200800	215000	93	N	14771	15900	93	N
Cr	1443	1235	117	N	3788	3795	100	N
Co	1016	1090	93	N	3462	3795	91	N
Cu	5313	5770	92	N	3577	3645	98	N
Fe	245343	253100	97	N	14633	15350	95	N
Pb	102269	89100	115	N	13201	15000	88	N
Mg	296800	302000	98	N	14343	15000	96	N
Mn	1755814	1740000	101	N	3186	3840	83	N
Mo	2117	2208	96	N	3654	3765	97	N
Ni	1435	1210	119	N	3770	3835	98	N
Se	7709	7870	98	N	15349	15600	98	N
Ag	996	986	101	N	2776	3925	71	N
Tl	6794	5495	124	N	13983	15300	91	N
V	1207	1255	96	N	3483	3660	95	N
Zn	8981	9295	97	N	3528.7	3850	92	N
Ba	9370	8940	105	N	3773.6	3645	104	N
Na	78600	73350	107	N	14371.4	13550	106	N
K	178800	160500	111	N	14600.0	13000	112	Y

TABLE 27. COMPARISON OF MSA AND NON-MSA RESULTS[a]

SPIKED BULK DIGESTS

		NON-MSA			MSA				
SAMPLE NAME	ELEMENT	N	MEAN CONC.[b]	SD	N	MEAN CONC.[b]	SD	%RATIO	SIG. DIF.[c]
HAZARDOUS WASTE	Cd	5	894	117	3	940	84	95	NO
HAZARDOUS WASTE	Tl	5	4410	788	3	4510	1130	98	NO
HAZARDOUS WASTE	Zn	5	4310	426	3	4560	250	95	NO
RIVER SEDIMENT	Tl	7	3160	2210	3	5050	675	63	NO
FLY ASH	Cd	5	754	422	3	897	219	84	NO
FLY ASH	Cr	5	1480	885	3	2390	1090	62	NO
FLY ASH	Pb	4	4100	634	4	6770	3300	61	NO
FLY ASH	Mn	4	1910	233	3	1750	304	109	NO
FLY ASH	Ni	3	1530	154	4	1350	500	113	NO
FLY ASH	Tl	4	5530	3730	3	1950	2470	284	NO
ESTUARINE SEDIMENT	Tl	5	3870	1290	3	3340	2850	116	NO
INDUSTRIAL SLUDGE	Tl	5	4470	872	3	4620	2230	97	NO
ELECTROPLATING SLUDGE	Tl	3	4600	740	4	5350	1120	86	NO
MINE TAILING	Cd	5	850	69	3	985	112	86	NO

[a] Only those elements that required the application of the MSA by three or more laboratories are included as statistically significant.

[b] Concentration for liquids in ug/L; concentration for solids in mg/kg.

[c] Result of a null hypothesis approach used to indicate whether MSA and non-MSA results are significantly different.

N - Number of cases.

% Ratio - non-MSA to MSA mean concentrations.

(continued)

TABLE 27. (continued)

UNSPIKED SOLIDS

SAMPLE NAME	ELEMENT	NON-MSA N	NON-MSA MEAN CONC.[b]	NON-MSA SD	MSA N	MSA MEAN CONC.[b]	MSA SD	%RATIO	SIG. DIF.[c]
HAZARDOUS WASTE	Be	4	0.8	0.1	3	0.7	0.2	93	NO
HAZARDOUS WASTE	Cr	6	95	8.4	3	111	10	86	YES
HAZARDOUS WASTE	Co	6	8.0	2.4	3	9.1	1.5	88	NO
HAZARDOUS WASTE (DUP.)	Ni	5	17	1.3	4	13	8.9	128	NO
RIVER SEDIMENT	Sb	6	325	266	3	169	246	192	NO
RIVER SEDIMENT	Cd	6	11	2.5	3	11	3.5	103	NO
RIVER SEDIMENT	Co	5	21	16	4	21	19	99	NO
RIVER SEDIMENT	Ni	6	44	20	3	27	7.0	161	NO
RIVER SEDIMENT (DUP.)	Cd	6	10	1.6	3	10	0.7	107	NO
RIVER SEDIMENT (DUP.)	Ni	6	39	13	3	38	19	105	NO
FLY ASH	Be	6	3.0	0.8	3	2.6	1.2	114	NO
MINE TAILING	Cd	4	2.3	1.6	3	1.9	1.1	122	NO
MINE TAILING	Zn	6	372	44	3	340	119	109	NO
MINE TAILING (DUP.)	Cd	4	2.4	1.6	3	1.5	0.8	158	NO
MINE TAILING (DUP.)	Co	6	7.3	2.5	3	8.8	3.1	83	NO
MINE TAILING (DUP.)	Ni	5	21	5.6	4	21	11	100	NO
MINE TAILING (DUP.)	Zn	6	365	43	3	345	122	106	NO
ELECTROPLATING SLUDGE	Cd	6	113	24	3	96	41	118	NO
ELECTROPLATING SLUDGE	Mn	6	226	31	3	254	126	89	NO
ELECTROPLATING SLUDGE (DUP.)	As	6	33	20	3	41	20	80	NO
ELECTROPLATING SLUDGE (DUP.)	Mo	5	14	11	3	21	7.3	68	NO
INDUSTRIAL SLUDGE	As	4	11	6.6	3	26	11	41	YES

(Continued)

TABLE 27. (concluded)

		NON-MSA			MSA				
SAMPLE NAME	ELEMENT	N	MEAN CONC.[b]	SD	N	MEAN CONC.[b]	SD	%RATIO	SIG. DIF.[c]
SPIKED SOLIDS									
HAZARDOUS WASTE	Co	6	45	8.2	3	30	2.2	149	YES
HAZARDOUS WASTE	Pb	6	340	104	3	238	14	143	NO
HAZARDOUS WASTE	Mo	6	39	20	3	29	2.8	134	NO
HAZARDOUS WASTE	Ni	6	57	10	3	37	2.9	152	YES
HAZARDOUS WASTE (DUP.)	Co	6	48	4.8	3	56	11	85	NO
HAZARDOUS WASTE (DUP.)	Pb	6	390	29	3	338	112	115	NO
HAZARDOUS WASTE (DUP.)	Ni	6	61	3.5	3	58	14	106	NO
ESTUARINE SEDIMENT	Cd	6	46	4.7	3	53	2.2	87	NO
ESTUARINE SEDIMENT	Mo	6	37	19	3	47	2.5	79	NO
ESTUARINE SEDIMENT	Ni	6	65	6.7	3	73	1.3	89	NO
ESTUARINE SEDIMENT	Tl	6	180	65	3	239	24	75	NO
ESTUARINE SEDIMENT (DUP.)	Ni	6	63	6.9	3	74	3.3	86	YES
MINE TAILING	Ni	6	64	7.9	3	60	15	108	NO
MINE TAILING (DUP.)	Ni	6	63	6.9	3	64	19	99	NO
ELECTROPLATING SLUDGE (DUP.)	Tl	6	160	46	3	304	104	53	YES

average analytical values for elements for the Method 6010 spiked bulk digests that required three or more MSA's (Table 7). These 14 values can be compared with the corresponding AAS results for accuracy, if it is assumed that the AAS values are the true values. This comparison shows that the application of the MSA increased the accuracy of the results eight times and decreased the accuracy of the results six times. In other words, on the average the application of the MSA leaves the overall data quality unchanged for this relatively small set of data.

National Bureau of Standards - Standard Reference Material - Method 3050/6010 UNSPIKED SOLIDS

Three of the solid materials used in this study are NBS-SRM's (see Table 1). The results of the Method 3050/6010 analysis of these three materials are shown in Tables 28 through 30 along with the "accepted results." In general, the Method 3050 digestion procedure extracted or leached variable amounts of each of the 23 elements from the three SRM's compared to the certified values.

Outliers - by Element and Laboratory

Outlier data, as determined by applying the Grubbs Test (3) to the reported data, are summarized by element, sample, and laboratory in Tables 31 through 33.

The fly ash Method 6010 spiked bulk digest, that contained high concentrations of added V and Mo, has the highest number of outliers; 16 out of a total of 184 reported values are outliers for this sample. However, the Electroplating Sludge Method 6010 spiked bulk digest has 15 outliers. The Hazard Waste No. 1 spiked bulk digest has the least outliers (eight) of the Method 6010 spiked bulk digests.

Outliers in the spiked and unspiked Method 3050/6010 spiked solids as in the Method 6010 spiked bulk digests do not indicate any trends by element, but Laboratory B has the highest number of outliers. In general, the total number of outliers is low, 228 out of the 7475 reported measurements, or 3 percent.

TABLE 28. COMPARISON OF METHOD 3050/6010 DATA WITH CERTIFIED VALUES FOR NBS COAL FLY ASH (SRM 1633_a)

Element	Method 3050/6010 Mean Concentration (mg/kg)	NBS Value[a,b] (mg/kg)	Method 3050/6010 Average as a Percent of NBS Value (%)
Al	15000	(140000)	(11)
Sb	12[c]	(7)	---
As	135.7	145	94
Be	2.9	(12)	(24)
Cd	1.8[d]	1.0	---
Ca	4670	11100	42
Cr	24.1	196	12
Co	10.9	(46)	(24)
Cu	30.5	118	26
Fe	18000	94000	19
Pb	27.8	72.4	38
Mg	772	4550	17
Mn	40.2	(190)	(21)
Mo	22.8	(29)	(79)
Ni	25.5	127	---
Se	40[e]	10.3	---
Ag	0.8[f]	---	---
Tl	10[g]	5.7	---
V	75.6	300	25
Zn	52.7	220	24
Ba	660	1500	44
Na	356	1700	21
K	1850	18800	10

[a] See reference 7.
[b] Parentheses indicate noncertified values.
[c] Eight laboratories reported Sb as not detected.
[d] Three laboratories reported Cd as not detected.
[e] Seven laboratories reported Se as not detected.
[f] Six laboratories reported Ag as not detected.
[g] Seven laboratories reported Tl as not detected.

TABLE 29. COMPARISON OF METHOD 3050/6010 DATA WITH CERTIFIED VALUES FOR NBS ESTUARINE SEDIMENTS (SRM 1646)

Element	Method 3050/6010 Mean Concentration (mg/kg)	NBS Value[a,b] (mg/kg)	Method 3050/6010 Averages as a Percent of NBS Value (%)
Al	15600	62500	25
Sb	11[c]	(0.4)	---
As	37[d]	11.6	---
Be	0.8	---	---
Cd	2.1	0.36	575
Ca	3590	8300	43
Cr	36.4	76	48
Co	9.4	10.5	90
Cu	12.7	18	71
Fe	24800	33500	74
Pb	31.8	28.2	113
Mg	7780	10900	71
Mn	207	375	55
Mo	3[e]	(2.0)	---
Ni	21.8	32	68
Se	20[f]	---	---
Ag	0.8[g]	---	---
Tl	13[h]	(0.5)	---
V	38.6	94	41
Zn	98.8	138	72
Ba	33.3	---	---
Na	9600	20000	48
K	3330	14000	24

[a] See reference 7.
[b] Parentheses indicate noncertified values.
[c] Seven laboratories reported Sb as not detected.
[d] Five laboratories reported As as not detected.
[e] Six laboratories reported Mo as not detected.
[f] Five laboratories reported Se as not detected.
[g] Six laboratories reported Ag as not detected.
[h] Seven laboratories reported Tl as not detected.

TABLE 30. COMPARISON OF METHOD 3050/6010 DATA WITH CERTIFIED VALUES FOR NBS RIVER SEDIMENT (SRM 1645)

Element	Method 3050/6010 Mean Concentration (mg/kg)	NBS Value[a,b] (mg/kg)	Method 3050/6010 Averages as a Percent of NBS Value (%)
Al	5060	22600	22
Sb	260	(51)	(510)
As	76[c]	(66)	--
Be	3.1	--	--
Cd	11.5	10.2	113
Ca	27000	(29000)	(93)
Cr	30200	29600	102
Co	18.5	10.1	183
Cu	89.7	109	82
Fe	81000	113000	72
Pb	630	714	88
Mg	6280	7400	85
Mn	621	785	79
Mo	15.4	--	--
Ni	38.4	45.8	84
Se	40[d]	1.5	---
Ag	1.3[e]	---	---
Tl	20[f]	1.44	---
V	15[g]	23.5	64
Zn	1550	1720	90
Ba	46.4	---	---
Na	1440	5400	27
K	450	12600	3.8

[a] See reference 7.

[b] Parenthesis indicates noncertified values.

[c] Three laboratories reported As as not detected.

[d] Four laboratories reported Se as not detected.

[e] Four laboratories reported Ag as not detected.

[f] Five laboratories reported Tl as not detected.

[g] Four laboratories reported V as not detected.

TABLE 31. OUTLIERS* OBSERVED IN METHOD 6010 SPIKED BULK DIGESTS AND METHOD 6010 QC SOLUTION DATA

OUTLIERS BY SAMPLE AND ELEMENT

	SAMPLE										
ELEMENTS	QC SOLN.	HAZ. WASTE	RIVER SED.	FLY ASH	EST. SED.	INDUST. SLUDGE	ELECT. SLUDGE	MINE TAILING	QC SOLN.	TOTAL	PERCENT
Al	0	0	0	0	2	1	0	2	0	5	7.0
Sb	0	0	0	2	0	1	1	1	0	5	7.0
As	1	0	1	0	1	0	1	1	0	5	7.0
Be	0	0	0	0	0	0	1	1	0	2	2.8
Cd	0	0	1	2	0	2	1	0	0	6	8.4
Ca	0	0	0	2	0	0	1	0	0	3	4.2
Cr	0	0	0	0	0	0	1	0	0	1	1.4
Co	0	0	0	1	0	0	1	0	0	2	2.8
Cu	0	1	1	2	2	0	0	1	0	7	9.8
Fe	0	0	1	0	0	0	1	0	0	2	2.8
Pb	1	0	1	1	2	1	1	2	0	9	13
Mg	0	0	0	0	0	1	0	0	0	1	1.4
Mn	0	0	0	1	0	1	1	0	0	4	5.6
Mo	0	1	0	0	0	1	0	0	0	2	2.8
Ni	1	0	1	2	0	1	1	0	0	6	8.4
Se	0	1	1	2	2	0	1	0	0	7	9.8
Ag	2	0	1	1	0	0	1	1	0	5	7.0
Tl	0	0	1	2	0	0	1	2	0	6	8.4
V	0	0	0	0	0	0	2	0	0	2	2.8
Zn	0	0	1	2	0	1	1	0	0	5	7.0
Ba	1	0	0	0	0	0	0	0	0	0	0.0
Na	0	0	0	0	0	2	0	0	0	2	2.8
K	0	0	0	0	1	0	0	0	0	1	1.4
TOTAL	6	3	10	20	10	12	16	11	0	88	5.4

* Outliers determined using Grubb's test at the 95 percent Confidence level.

(continued)

TABLE 31. (concluded)

OUTLIERS BY LABORATORY AND SAMPLE

	SAMPLE										
LABORATORY	QC SOLN.	HAZ. WASTE	RIVER SED.	FLY ASH	EST. SED.	INDUST. SLUDGE	ELECT. SLUDGE	MINE TAILING	QC SOLN.	TOTAL	PERCENT
A	1	0	2	1	0	0	1	0	0	5	2.7
B	1	0	1	5	2	1	3	3	0	16	8.7
C	2	2	2	2	2	4	6	1	0	21	11
E	0	0	1	2	2	2	6	1	0	14	7.6
F	1	1	2	0	1	0	1	1	0	7	3.8
G	0	0	2	3	1	3	0	1	0	10	5.4
H	0	0	0	2	2	2	0	1	0	7	3.8
I	1	0	0	4	1	0	1	2	0	9	4.9

TABLE 32. OUTLIERS* OBSERVED IN METHOD 3050/6010 UNSPIKED SOLIDS DATA

OUTLIERS BY SAMPLE AND ELEMENT

	SAMPLE															
	ELECTRO SLUDGE		HAZ. WASTE		RIVER SED.		FLY ASH		INDUST. SLUDGE		MINE TAILING		EST. SEDIMENT			
ELEMENT	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	TOTAL	PERCENT
Al	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sb	0	0	0	0	0	0	1	1	1	1	1	1	1	1	8	6.3
As	0	0	0	0	0	0	0	0	2	1	0	0	2	2	7	5.6
Be	1	0	0	0	0	0	0	0	1	0	0	0	1	0	3	2.3
Cd	0	1	0	0	0	0	0	0	0	1	0	0	0	0	1	0.8
Ca	1	0	1	0	0	0	0	0	1	0	0	0	0	0	3	2.4
Cr	1	1	0	0	0	0	0	0	0	0	2	0	0	0	4	3.2
Co	1	2	0	1	0	1	0	0	0	0	0	0	1	1	5	4.0
Cu	0	0	0	0	0	0	0	0	0	0	1	1	0	0	2	1.6
Fe	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Pb	0	2	0	0	0	0	0	0	0	0	1	0	0	0	4	3.2
Mg	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0.8
Mn	0	0	0	0	0	0	0	1	0	0	1	0	0	0	3	2.4
Mo	0	0	0	0	0	0	1	1	0	0	0	0	0	0	2	1.6
Ni	1	0	0	0	1	0	0	0	0	0	0	0	0	0	2	1.6
Se	0	0	0	0	0	0	3	1	0	0	0	0	1	1	6	4.8
Ag	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tl	0	1	0	0	1	1	0	0	0	1	0	0	1	1	7	5.6
V	1	0	0	1	0	0	0	0	0	0	0	0	0	0	2	1.6
Zn	0	0	0	1	1	0	0	0	0	0	0	0	0	0	3	2.4
Ba	0	0	1	1	0	0	1	0	0	1	0	1	0	0	4	3.2
Na	0	0	0	0	0	0	2	2	1	1	0	0	0	0	6	4.8
K	0	0	0	1	0	0	0	0	0	0	1	0	0	0	2	1.6
TOTAL	5	8	2	5	3	5	8	6	5	5	7	3	8	6	76	2.5

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* Outliers determined using Grubb's test at the 95 percent Confidence level.

(continued)

TABLE 32. (concluded)

OUTLIERS BY LABORATORY AND SAMPLE

SAMPLE

	ELECTRO SLUDGE		HAZ. WASTE		RIVER SED.		FLY ASH		INDUST. SLUDGE		MINE TAILING		EST. SEDIMENT			
LABORATORY	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	TOTAL	PERCENT
A	1	2	0	0	1	1	0	1	0	2	0	0	1	2	11	3.4
B	1	1	1	2	1	5	3	3	3	2	2	1	1	1	27	8.4
C	1	1	0	0	0	0	1	1	1	1	1	0	1	1	9	2.8
D	1	1	0	0	0	1	1	0	0	0	0	1	0	0	5	1.5
E	0	1	0	0	0	0	1	1	1	0	2	0	1	1	8	2.5
F	0	1	0	0	1	1	0	0	0	0	0	1	0	1	5	1.6
G	1	0	1	1	0	0	1	0	0	0	0	0	1	0	5	1.6
H	0	1	0	1	0	1	0	0	0	0	0	0	0	1	4	1.2
I	1	1	0	0	0	0	1	0	1	0	2	1	1	1	7	2.2
TOTAL	6	9	2	4	3	9	8	6	6	5	5	4	6	8	81	2.8

TABLE 33. OUTLIERS* OBSERVED IN METHOD METHOD 3050/6010 SPIKED SOLIDS DATA

OUTLIERS BY SAMPLE AND ELEMENT

	SAMPLE															
	ELECTRO SLUDGE		HAZ. WASTE		RIVER SED.		FLY ASH		INDUST. SLUDGE		MINE TAILING		EST. SEDIMENT			
ELEMENT	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	TOTAL	PERCENT
Al	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0.8
Sb	0	0	1	1	0	0	0	0	0	0	0	1	0	0	3	2.4
As	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0.8
Be	1	1	0	0	0	0	0	0	0	0	1	1	0	0	2	1.6
Cd	0	0	0	0	1	1	1	0	0	0	0	0	0	0	3	2.4
Ca	0	0	1	0	0	0	0	0	0	1	0	0	0	1	3	2.4
Cr	0	0	1	0	2	0	0	0	0	0	1	1	0	0	5	4.0
Co	0	2	0	0	0	0	0	0	0	0	0	2	0	1	3	2.4
Cu	1	0	0	1	0	0	1	0	0	0	1	1	0	1	6	4.8
Fe	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0.8
Pb	0	0	1	0	0	0	0	0	0	0	1	1	0	1	4	3.2
Mg	0	0	0	0	0	0	0	0	0	1	0	0	0	1	2	1.6
Mn	0	0	0	1	0	1	1	1	0	1	0	0	0	1	6	4.8
Mo	0	0	1	1	0	0	0	0	1	1	0	1	1	2	7	5.6
Ni	2	0	0	1	0	0	0	0	0	0	0	0	0	1	4	3.2
Se	0	0	0	1	1	1	1	0	0	0	0	2	0	1	7	5.6
Ag	2	2	1	1	0	2	0	0	0	2	0	1	0	0	11	8.7
Tl	0	0	0	0	0	0	0	1	1	0	0	1	0	0	3	2.4
V	0	0	0	0	0	2	0	0	0	0	0	0	0	1	3	4.1
Zn	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ba	0	0	0	0	0	0	0	0	1	0	1	0	0	0	2	1.6
Na	1	0	2	0	0	0	0	0	0	1	0	0	0	1	5	4.0
K	1	1	0	0	0	0	0	0	0	0	0	0	0	1	4	3.2
TOTAL	7	7	8	6	4	7	4	2	3	7	4	9	1	13	84	2.9

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[*] Outliers determined using Grubb's test at the 95 percent confidence level.

(continued)

TABLE 33. (concluded)

OUTLIERS BY LABORATORY AND ELEMENT

	SAMPLE															
	ELECTRO SLUDGE		HAZ. WASTE		RIVER SED.		FLY ASH		INDUST. SLUDGE		MINE TAILING		EST. SEDIMENT			
LABORATORY	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	TOTAL	PERCENT
A	0	0	0	0	0	0	1	1	0	0	0	0	0	0	2	0.6
B	2	0	1	0	1	0	0	1	1	7	0	0	0	13	26	8.1
C	0	0	1	0	1	1	0	0	1	1	0	0	1	1	7	2.2
D	4	2	2	1	1	1	0	0	0	1	1	0	0	0	13	4.0
E	0	0	1	0	1	0	0	0	0	0	1	2	2	0	7	2.2
F	0	1	1	1	1	1	0	0	0	0	0	1	0	0	6	1.9
G	1	3	1	1	2	1	0	0	1	0	1	3	1	0	14	4.3
H	1	1	1	0	1	1	1	0	0	1	0	1	1	0	9	2.8
I	0	0	1	1	1	0	0	0	0	0	1	2	0	0	7	2.2
TOTAL	8	7	9	4	9	5	2	2	3	10	4	9	2	14	91	3.1

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APPENDIX A
METHOD 6010

INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma optical emission spectroscopy (ICP) determines metals in solution. The method is applicable to a large number of metals and wastes. All matrices including groundwater, aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis.

1.2 Elements for which Method 6010 is applicable are listed in Table 1. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 1 provide concentration ranges for clean aqueous samples. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested by procedures presented in Methods 3005, 3010, 3020, 3030, 3040, and 3050.

2.2 Method 6010 describes the simultaneous, or sequential, multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Metal-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 3.0 (and tests for their presence as described in 7.5) should also be recognized and appropriate corrections made.

3.0 INTERFERENCES

3.1 Spectral interferences are (1) overlap of a spectral line from another element, (2) unresolved overlap of molecular bank spectra, (3) background contribution from continuous or recombination phenomena, and (4) stray

TABLE 1. RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength[a] (nm)	Estimated Detection Limit[b] (μg/L)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	see *
Selenium	196.026	75
Silicon	288.158	27
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[a] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see 3.1). In time, other elements may be added as more information becomes available and as required.

[b] The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

*Highly dependent on operating conditions and plasma position.

light from the line emission of high concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. The third and fourth effects can usually be compensated for by a background correction adjacent to the analyte line. Users of simultaneous multielement instruments must verify the absence of spectral interference from an element in a sample for which there is no channel in the instrument detection. Interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as a rudimentary guide for indicating potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

3.1.1 The interference is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/l of the interference element. For example, assume that arsenic is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/l of aluminum. According to Table 2, 100 mg/l of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/l. Therefore, 10 mg/l of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/l. The reader is cautioned that other analytical systems will exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual system.

3.1.2 The blank spaces in Table 2 indicate that no measurable interferences were observed for the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

3.1.3 At present, information on the listed silver and potassium wavelengths is not available but it has been reported that second-order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Change in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, using a peristaltic pump or the standard addition method. Another problem that can occur from high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.

TABLE 2. ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM INTERFERENCES AT THE 100-mg/l LEVEL

		Interferent (mg/l)									
Analyte	Wavelength (nm)	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Boron	249.773	0.04	--	--	--	0.32	--	--	--	--	--
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Silicon	288.158	--	--	0.07	--	--	--	--	--	--	0.01
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

TABLE 3. ANALYTE AND INTERFERENCE ELEMENTAL CONCENTRATIONS USED FOR INTERFERENCE MEASUREMENTS IN TABLE 2

Analytes	mg/l	Analytes	mg/l	Interferents	mg/l
Al	10	Mn	1	Al	1,000
As	10	Mo	10	Ca	1,000
B	10	Na	10	Cr	200
Ba	1	Ni	10	Cu	200
Be	1	Pb	10	Fe	1,000
Ca	1	Sb	10	Mg	1,000
Cd	10	Se	10	Mn	200
Co	1	Si	1	Tl	200
Cr	1	Tl	10	V	200
Cu	1	V	1		
Fe	1	Zn	10		
Mg	1				

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not pronounced with the ICP technique. If observed they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and specific analyte element.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled plasma-atomic emission spectrometer.

4.1.1 Computer-controlled atomic emission spectrometer with background correction.

4.1.2 Radio frequency generator.

4.1.3 Argon gas supply, welding grade or better.

4.2 Operating conditions: The analyst should follow the instructions provided by the instrument's manufacturer. For operation with organic solvents, use of the auxiliary argon inlet (at 1 l/min) is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

5.0 REAGENTS

5.1 *Acids* used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

5.1.1 Acetic acid, conc.

5.1.2 Hydrochloric acid, conc.

5.1.3 Hydrochloric acid (1:1): Add 500 ml conc. HCl to 400 ml Type II water and dilute to 1 liter.

5.1.4 Nitric acid, conc.

5.1.5 Nitric acid (1:1): Add 500 ml conc. HNO_3 to 400 ml Type II water and dilute to 1 liter.

5.2 *Type II water*: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use Type II water for the preparation of all reagents and calibration standards, and as dilution water. The purity of this water must be equivalent to or better than ASTM type II reagent water of Specification D1193.

5.3 *Standard stock solutions* may be purchased or prepared from ultra-high purity grade chemicals or metals. All salts must be dried for 1 hr at 105°C unless otherwise specified. (CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow.

5.3.1 Aluminum solution, stock, 1 ml = 100 µg Al: Dissolve 0.100 g of aluminum metal in an acid mixture of 4 ml of (1:1) H01 and 1 ml of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask and add an additional 10 ml of (1:1) HCl and dilute to 1,000 ml with Type II water.

5.3.2 Antimony solution, stock, 1 ml = 100 µg Sb: Dissolve 0.2669 g $K(SbO)c_4H_4O_6$ in Type II water, add 10 ml (1:1) HCl and dilute to 1,000 ml with Type II water.

5.3.3 Arsenic solution, stock, 1 ml = 100 µg As: Dissolve 0.1320 g of As_2O_3 in 100 ml of Type II water containing 0.4 g NaCH. Acidify the solution with 2 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.4 Barium solution, stock, 1 ml = 100 µg Ba: Dissolve 0.1516 g $BaCl_2$ (dried at 250°C for 2 hr) in 10 ml Type II water with 1 ml (1.1) HCl. Add 10.0 ml (1:1) HCl and dilute to 1,000 ml with Type II water.

5.3.5 Beryllium solution, stock, 1 ml = 100 µg Be: Do not dry. Dissolve 1.966 g $BeSO_4 \cdot 4H_2O$ in Type II water, add 10.0 ml conc. ENO_3 and

dilute to 1,000 ml with Type II water.

5.3.6 Boron solution, stock, 1 ml = 100 µg B: Do not dry. Dissolve 0.5716 g anhydrous H_3BO_3 in Type II water and dilute to 1,000 ml. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered, and store in a desiccator to prevent the entrance of atmospheric moisture.

5.3.7 Cadmium solution, stock, 1 ml = 100 µg Cd: Dissolve 0.1142 g CdO in a minimum amount of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.8 Calcium solution, stock, 1 ml = 100 µg Ca: Suspend 0.2498 g $CaCO_3$ dried at 180°C for 1 hr before weighing in Type II water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.9 Chromium solution, stock, 1 ml = 100 µg Cr: Dissolve 0.1923 g CrO_3 in Type II water. When solution is complete, acidify with 10 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.10 Cobalt solution, stock, 1 ml = 100 µg Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1:1) HNO_3. Add 10.0 ml (1:1) HCl and dilute to 1,000 ml with Type II water.

5.3.11 Copper solution, stock, 1 ml = 100 µg Cu: Dissolve 0.1252 g CuO in a minimum amount of (1:1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.12 Iron solution, stock, 1 ml = 100 µg Fe: Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 ml (1:1) HCl and 2 ml of conc. HNO_3. Cool, add an additional 5.0 ml of conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.13 Lead solution, stock, 1 ml = 100 µg Pb: Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1:1) HNO_3. Add 10 ml (1:1) HNO_3 and dilute to 2,000 ml with Type II water.

5.3.14 Magnesium solution, stock, 1 ml = 100 µg Mg: Dissolve 0.1658 g MgO in a minimum amount of (1:1) HNO_3. Add 10.0 ml (1:1) conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.15 Manganese solution, stock, 1 ml = 100 µg Mn: Dissolve 0.1000 g of manganese metal in the acid mixture (10 ml conc. HCl and 1 ml conc. HNO_3) and dilute to 1,000 ml with Type II water.

5.3.16 Molybdenum solution, stock, 1 ml = 100 µg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in Type II water and dilute to 1,000 ml with Type II water.

5.3.17 Nickel solution stock, 1 ml = 100 µg Ni: Dissolve 0.1000 g of nickel metal in 10.0 ml hot conc. HNO_3, cool, and dilute to 1,000 ml with Type II water.

5.3.18 Potassium solution, stock, 1 ml = 100 µg K: Dissolve 0.1907 g KOl, dried at 110°C, in Type II water and dilute to 1,000 ml.

5.3.19 Selenium solution, stock, 1 ml = 100 µg Se: Do not dry. Dissolve 0.1727 g H_2SeO_3 in Type II water and dilute to 1,000 ml.

5.3.20 Silicon solution, stock, 1 ml = 100 µg Si: Do not dry. Dissolve 1.0118 g $Na_2SiO_3 \cdot 9H_2O$ in Type II water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.21 Silver solution stock, 1 ml = 100 µg Ag: Dissolve 0.1575 g $AgNO_3$ in Type II water and 10 ml conc. HNO_3. Dilute to 1,000 ml with Type II water.

5.3.22 Sodium solution, stock, 1 ml = 100 µg Na: Dissolve 0.2542 g NaCl in Type II water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.23 Thallium solution, stock, 1 ml = 100 µg Tl: Dissolve 0.1303 g $TlNO_3$ in Type II water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.3.24 Vanadium solution, stock, 1 ml = 100 µg V: Dissolve 0.2297 g NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc HNO_3 and dilute to 1,000 ml with Type II water.

5.3.25 Zinc solution, stock, 1 ml = 100 µg Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with Type II water.

5.4 Mixed calibration standard solutions: Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 4). Add 2 ml of (1:1) HNO_3 and 10 ml of (1:1) HCl and dilute to 100 ml with Type II water (see NOTE below). Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to a FEP fluorocarbon or unuseed polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (see 5.8). Some typical calibration standard combinations are listed in Table 4.

TABLE 4. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, Se, and Si
IV	Al, Ca, Cr, K, Na, and Ni
V	Ag*, B, Mg, Sb, and Tl

*See NOTE.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 ml of Type II water and warm the flask until the solution clears. Cool and dilute to 100 ml with Type II water. For this acid combination, the silver concentration should be limited to 2 mg/l. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

5.5 Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve while the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by diluting 2 ml of (1:1) HNO_3 and 10 ml of (1:1) HCl to 100 ml with Type II water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

5.5.2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The instrument check standard is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves (see 7.6.2.1).

5.7 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of 10 times the instrumental detection limits. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero.

5.8 The quality control sample should be prepared in the same acid matrix as the calibration standards at 10 times the instrumental detection limits and in accordance with the instructions provided by the supplier.

6.0 PROCEDURE

6.1 Preliminary treatment of all matrices is always necessary because of the complexity and variability of sample matrices. Solubilization and digestion procedures are presented in Methods 3005, 3010, 3020, 3030, 3040, and 3050.

6.2 Set up instrument with proper operating parameters established in Section 4.2. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration.

6.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 5.4. Flush the system with the calibration blank (5.5.1) between each standard (see NOTE below). (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

NOTE: For boron concentrations greater than 500 µg/liter, extended flush times of 1 to 2 min may be required.

6.5 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than ±10% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

6.6 Flush the system with the calibration blank solution for at least 1 min (5.5.1) before the analysis of each sample (see preceding NOTE). Analyze the instrument check standard (5.6) and the calibration blank (5.5.1) after each 10 samples.

6.7 Calculations: Reagent blanks (5.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion. If dilutions were performed, the appropriate factor must be applied to sample values. All results should be reported in mg/l with up to three significant figures. Use MSA per 7.6.5.

7.0 QUALITY CONTROL

7.1 All quality control data should be maintained and available for easy reference or inspection.

7.2 Dilute and reanalyze samples that are more concentrated than the linear calibration limit, unless the equation used in standardization includes terms for nonlinear calibration.

7.3 Employ a minimum of one procedural blank per sample batch to determine if contamination or any memory effects are occurring.

7.4 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

7.5 It is recommended that, whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 7.5.1 through 7.5.3, will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

7.5.1 Serial Dilution: If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 10% of the original determination (or within some acceptable control limit that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

7.5.2 Spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 90 to 110% of the known value (or within the established control limits for a matrix). The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit or 1 mg/l, whichever is larger. If the spike is not recovered within the specified limits, a matrix effect should be suspected. The use of a standard-addition analysis procedure can usually compensate for this effect. CAUTION: The standard-addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

7.5.3 Standard addition: The standard-addition technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution, each of Volume V_x, are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

$$c_x = \frac{S_B V_s c_s}{(S_A - S_B)\, V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x, and thus c_s is much greater than c_x, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results for this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same way as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

7.6 Check the instrument standardization by analyzing appropriate quality-control check standards as follows.

7.6.1 Calibrate instrument using a minimum of three calibration blanks (5.5.1) and two point standard curve. Determine a mean background level and the standard deviation using the three calibration blanks.

7.6.2 Verify calibration at the beginning and end of an analytical run and every 20 samples. Calibration may be verified using a calibration blank (5.5.1) and a single point check standard (5.6).

7.6.2.1 The results of the check standard are to agree within ±10% of the expected value; if not, analysis is terminated, the problem is corrected, and the instrument is recalibrated.

7.6.2.2 The results of the calibration blank are to agree within three standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, and recalibrate.

7.6.3 Verify the interelement and background correction factors at the beginning and end of an analytical run and every 20 samples. Do this by analyzing the interference check sample (5.7). Results should be within three standard deviations of the mean value obtained during standardization.

7.6.4 A duplicate and a matrix spike addition is to be analyzed every 10 samples, batch or matrix type.

7.6.4.1 The relative percent difference between duplicate analyses is to be calculated as follows:

$$RPD = \frac{D_1 - D_2}{\frac{D_1 + D_2}{2}} \times 100$$

where:

RPD = relative percent difference
D_1 = first sample value
D_2 = second sample value (duplicate).

A control limit of ±20% for RPD shall be used for sample values greater than 10 times the detection limit.

7.6.4.2 The matrix spike recovery is to be within ±25% of the actual value.

7.6.5 The method of standard addition (MSA; 7.5.3) shall be used for the analysis of all EP extracts and sample digests unless it can be verified by serial dilution or matrix spike addition that MSA is not required.

8.0 PERFORMANCE

8.1 In an EPA round-robin phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 5 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.0 REFERENCES

American Society for Testing and Materials, Method D1193.

TABLE 5. ICP PRECISION AND ACCURACY DATA[a]

	Sample No. 1			Sample No. 2			Sample No. 3		
Element	True Value (µg/l)	Mean Reported Value (µg/l)	Mean SD[b] (%)	True Value (µg/l)	Mean Reported Value (µg/l)	Mean SD[b] (%)	True Value (µg/l)	Mean Reported Value (µg/l)	Mean SD[b] (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	700	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	32	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

[a] Not all elements were analyzed by all laboratories.
[b] SD = standard deviation.

APPENDIX B
METHOD 3050

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled plasma optical emission spectroscopy (ICP). Samples prepared by this method may be analyzed by AAS or ICP for the following elements:

- Aluminum
- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Calcium
- Chromium
- Cobalt
- Copper
- Iron
- Lead
- Magnesium
- Manganese
- Molybdenum
- Nickel
- Potassium
- Selenium
- Silver
- Sodium
- Thallium
- Vanadium
- Zinc

2.0 SUMMARY OF METHOD

> NOTE: A different digestion procedure is required for furnace AAS than for the non-furnace techniques because of the volatility of chloride salts.

2.1 A representative 1- to 2-g (wet weight) portion of the sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for (1) the furnace AAS analysis for Sb and for (2) the flame AAS or ICP analysis for Al, Sb, As, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, MN, Mo, Ni, K Se, Ag, Na, Tl, V, and Zn. Nitric acid is employed as the final reflux acid for the furnace AAS analysis for Al, As, Ba, Be, Ca, Cd, Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Ag, Na, Tl, V, and Zn. A separate portion of the sample shall be dried for a total solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste. Nondestructive techniques such as neutron activation analysis may also be helpful in evaluating the applicability of this digestion method.

4.0 APPARATUS AND METERIALS

4.1 125-ml conical phillips' beakers.

4.2 Watch glasses.

4.3 Drying ovens that can be maintained at 30°C.

4.4 Thermometer that covers range of 0 to 200°C/

4.5 Whatman No. 42 filter paper or equivalent.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.3 Concentrated hydrochloric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.4 Hydrogen peroxid (30%): Oxidant should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Nonaqueous samples shall be refrigerated upon receipt, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Mix the sample throughly to achieve homogeneity. For each digestion procedure, weigh and transfer tc a conical beaker at 1.00- to 2.00-g portion (to the nearest 0.01 g) of sample.

7.2 Add 10 ml of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 ml of concentrated HNO_3, replace the watch glass, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.

7.3 After the second reflux step has been completed and the sample has cooled, add 2 ml of Type II water and 3 ml of 30 percent hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

7.4 Continue to add 30 percent H_2O_2 in 1-ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 ml or 30 percent H_2O_2.)

7.5 If the sample is being prepared for (a) the furnace AAS analysis for Sb or for (b) the flame AAS or ICP analysis for Al, Sb, As, BA, Be, Ca, Cd. Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se, Ag, Na, Tl, V, and Zn then add 5 ml of 1:1 HCl and 10 ml of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted sample has an approximate acid concentration of 2.5 percent (v/v) HCl and 5 percent (v/v) HNO_3. The sample is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis for As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se, Ag, Na, Tl, V, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 ml, add 10 ml of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted digestate solution contains approximately 2 percent (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

7.7 To determine the percent solids in the sample material, add a separate portion of the wet sample to a tared weighing dish. Weigh the record the weight of the dish with the wet aliquot and lid. Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven that is set at 103-115°C. Perform this task in a well-ventilated area. Dry the sample to constant weight. Cool the sample in a desiccator with the weighing dish cover in place before each weighing. Record each weight. Do not analyze this dried portion of sample for the elements.

8.0 QUALITY CONTROL

8.1 For each group of samples processed, procedural blanks (Type II water and reagents) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 10 percent is recommended.

8.3 Spiked samples, measurements by another technique, and/or standard reference materials must be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality-control check sample obtained from an outside source.

8.5 The method of standard additions (MSA) shall be used unless it can be verified by serial dilution or matrix spike addition that MSA is not required.

9.0 CALCULATIONS

9.1 A separate determination of percent solids must be performed on a homogeneous aliquot of the sample

9.2 The concentrations determined are to be reported on the basis of dry weight of the sample.

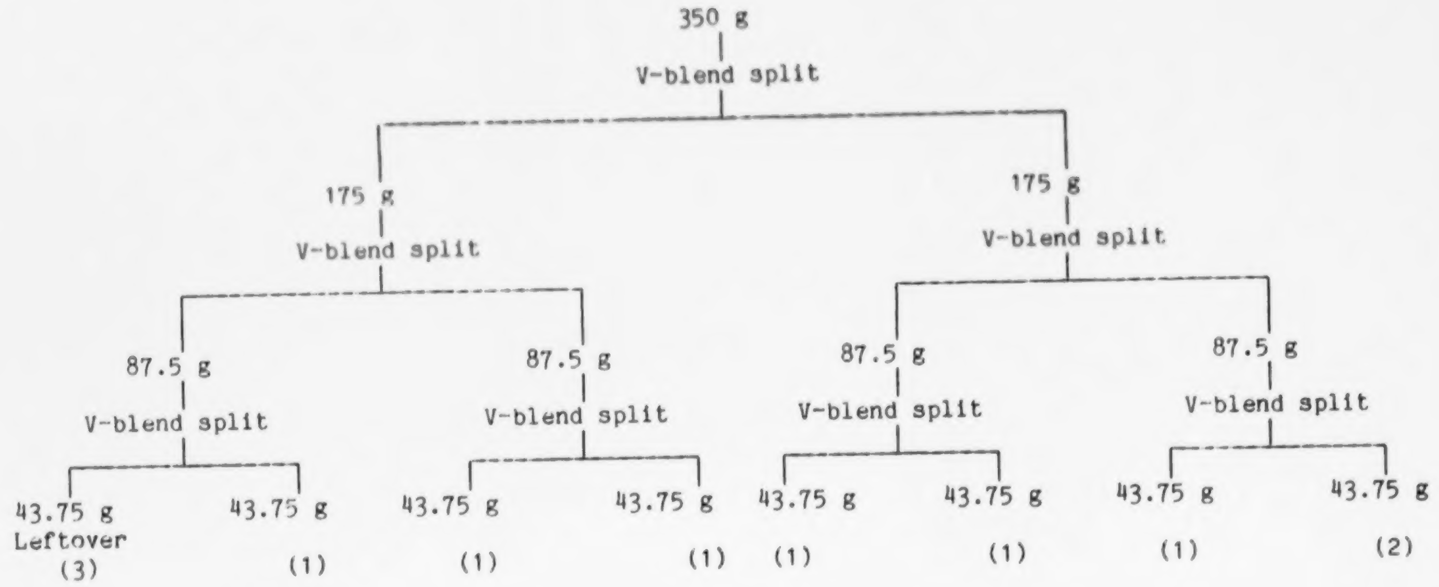
$$\text{Concentration in mg/kg (dry wt.)} = \frac{C \times V}{W \times S}$$

where C = Concentration (mg/l)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample
S = % Solids/100

APPENDIX C
METHOD 3050/6010 PERFORMANCE EVALUATION MATERIAL HOMOGENIETY STUDY

SAMPLE PREPARATION

Each of the seven samples was rehomogenized by blending them in a V-blender for one hour. Thirteen 24-gram aliquots were prepared according to the scheme shown in Figure 1. Each of the fractions shown in Figure 1 was split as follows. Each fraction was placed in the V-blender and blended for about 10 minutes. The blender was stopped with the point of V facing up. The ports at the bottom of each half of the V were then opened to split the material originally placed in the V into two equal parts. When the quantity in each aliquot was reduced to 43.75 grams, the total amount of material was too small to ensure reliable splitting with the V-blender. Seven of the eight 43.75 gram aliquots were split into fourteen 21.5 gram aliquots by alternately spooning material into two containers. One of the fourteen 21.5 gram aliquots was picked at random and the material was added to the unsplit 43.75 gram aliquot to generate a "leftover" fraction. Material from the leftover fraction was then added to each of the thirteen 21.5 gram analytical fractions to bring the weight of analytical fraction to 24 grams.


350 g
V-blend split
175 g
V-blend split
175 g
V-blend split
87.5 g
V-blend split
87.5 g
V-blend split
87.5 g
V-blend split
87.5 g
V-blend split
43.75 g
Leftover
(3)
43.75 g
(1)
43.75 g
(1)
43.75 g
(1)
43.75 g
(1)
43.75 g
(1)
43.75 g
(1)
43.75 g
(2)

(1) Split manually using spoon method into 12 samples of 21.88 g each.

(2) Split manually into two samples of 21.88 g each. One of the samples was added to the leftover.

(3) Material from leftover added to each of the thirteen 21.88 gm samples to make 24 gms.

Figure 1. Preparation of samples.

Before randomly picking samples for digestion and analysis, each bottle was numbered one to thirteen. The bottle numbers were carried throughout the analysis and data workup.

SELECTION OF SAMPLES FOR ANALYSIS

To study both the sampling and subsampling (inter- and intra-bottle) homogeneity of each of seven samples, it was necessary to analyze aliquots both from different bottles and from the same sample bottle. Five of the thirteen bottles were picked at random for ICP analysis. Then, three of these five bottles were picked for duplicate analysis. A 4-g aliquot was used for each analysis by Method 3050/6010.

SOLID SAMPLE DIGESTION AND ANALYSIS FOR VERIFICATION OF HOMOGENEITY

Four gram aliquots were digested using the Method 3050 digestion protocol as modified by the EPA EMSL-LV for this subtask. In addition to the seven samples, a blank and a Three Kids Mine (TKM-85) solid laboratory control sample were run with each digestion. The TKM-85 sample was digested and run to provide a UNLV-QAL digestion QC sample.

The digested samples were analyzed on a ARL 35000 ICP (sequential type) using Method 6010. A three-point calibration curve was used for quantitation. The level of QC used to ensure the reliability of the results was extensive. The ratio of QC runs to analytical runs was approximately 1:1. Typically, about 20 calibration or QC runs were made before sample analysis was begun. QC samples were run after every ten samples and QC samples were run after a set of analyses was complete. The run list shown in Table 2 gives an indication of the number and type of QC samples run. The method of standard additions and/or spiking of the low-level solutions were not applied for the homogeneity study.

The statistical report on homogeneity is given in Attachment A. In summary, the samples were relatively uniform with respect to the inter- and intra-sample aliquots. Only the level of silver in aliquot 12-D of the "Hazardous Waste 1" sample appeared to be anomalous. This aliquot was one of the duplicates and there is a very significant difference between the results for Sample 12 (0.043) and for 12-D (1.411). The value for aliquot 12-D meets all acceptance requirements, and it was verified by reanalysis of the digest. This anomaly may represent a local inhomogeneity.

TABLE 2. ANALYTICAL RUN SEQUENCE FOR ICP ANALYSES

1-3. 2% nitric acid
4. 2% nitric acid
5. Standard #3
6. Standard #5
7. WS378 QC solution
8. TM1-2 QC solution
9. TM3-2 QC solution
10-13. ICV #1, #2, #3, and #4 QC solutions
14. ICS X-85
15. 2% nitric acid
16. Standard #3
17. Standard #5
18-27. Ten analytical runs
28. 2% nitric acid
29. Standard #3
30. Standard #5
31-40. Ten analytical runs

N-11. TKM
N-10. 1:4 dilution of TKM
N-9. 1:16 dilution of TKM
N-8. 1:64 dilution of TKM
N-7. 2% nitric acid
N-6. Standard #3
N-5. Standard #5
N-4. ICS X-85
N-3. Al - 1000 ppm
N-2. Fe - 1000 ppm
N-1. Mn - 250 ppm
N. Cr - 250 ppm

APPENDIX C

ATTACHMENT 1

DATA ANALYSIS

An important initial question in this work was whether the aliquots drawn from each of the seven sludges were homogeneous (i.e., did the aliquots from a particular sludge all have the same concentrations for each of the 23 elements being measured). To determine the answer to this question variance components analyses were run on measurements from subsamples from 5 randomly chosen aliquots from each of the 7 sludges for each of the 23 elements. Two subsamples were analyzed from each of three of the chosen aliquots within a sludge, and one subsample was analyzed from the other two aliquots. (There was one exception where three subsamples were analyzed from one aliquot of the River Sediment because the analyst thought the analysis on the first subsample was too different from that on the second. The third subsample was only analyzed for the first 20 elements. Data from all three of the subsamples were used in the variance components analysis.)

In a variance components analysis, it is important that the variances not be functions of the means of the variables being measured. An investigation of the raw data indicated that the standard deviation was approximately proportional to the mean (i.e., an approximately constant coefficient of variation), and this indicated that a logarithmic transformation would be needed to stabilize the variance. Hence, the variance components analysis for each of the 23 elements was performed on (natural) log-transformed data. The model for the variance components analysis has equation,

$$Y_{ijk} = \mu + \alpha_i + \beta_{ij} + \epsilon_{ijk}$$

where under the model Y_{ijk} is a random variable representing the measurement of an element on subsample k from aliquot j of sludge i, μ represents an unknown mean concentration over all sludges, α_i is a random variable with mean 0 and variance $\sigma_A{}^2$ representing the difference between the concentration of sludge i and μ, β_{ij} is a random variable with mean 0 and variance $\sigma_B{}^2$ representing the difference between the mean concentration of sludge i (namely, $\mu + \alpha_i$) and the concentration of the element in aliquot j from sludge i, and ϵ_{ijk} is a random variable with mean 0 and variance $\sigma_E{}^2$ representing the difference between the measured concentration of subsample k and the true concentration in the aliquot $(\mu + \alpha_i + \beta_{ij})$. If adequate mixing has been done prior to drawing of the aliquots, the values of the β_{ij} and of $\sigma_B{}^2$ should be essentially 0.

The results of the 23 variance components analyses on the log-transformed data are given in Table 1. The estimates of $\sigma_E{}^2$ and $\sigma_B{}^2$ are given in the "Error Variance" and "Between Variance" columns of the table. Table 1 shows that in 12 of the 23 analyses, the maximum likelihood estimator of $\sigma_B{}^2$ returned a negative value (since variances cannot be negative, the value reported by the BMDP[1] computer program is 0). This means that the median of the 23 estimates of the variances between aliquots not greater than zero and so our estimate of this variance is zero. Only one estimate of the variance between aliquots was large with respect to its standard error and with respect to the error variance for measurements of the element. With 23 estimates it is not unexpected that at least one estimate will appear significantly large.

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[1] BMDP Statistical Software. University of California Press, Berkeley, CA 94720.

Under the assumption that mixing was adequate and that σ_B^2 is 0, all measurements on a sludge carry equal weight in estimating the concentration of an element in the sludge. A table of summary statistics for the concentrations of the various elements in the seven sludges is given in Table 2 where the standard deviation is based on all measurements (except possibly some outliers).

TABLE 1. ESTIMATED VARIANCE COMPONENTS[1] IN HOMOGENEITY STUDY

Element	Error Variance[2]	Between Variance[3]	Standard Error[4,5]	Data Quality[6]	Comments
Al	0.0060	0.00056	0.0015	5	
Sb	.0456	.02536	.0175	6	A
As	.1414	.00000	.0000	6	B
Be	.0032	.00123	.0011	6	C
Cd	.0162	.00000	.0000	6	D
Ca	.0013	.00000	.0000	5	
Cr	.0055	.00090	.0015	5	
Co	.1042	.03325	.0323	6	
Cu	.0036	.00000	.0000	5	
Fe	.0058	.00000	.0000	5	
Pb	.0071	.00003	.0017	5	
Mg	.0010	.00000	.0000	5	
Mn	.0012	.00000	.0000	5	
Mo	.0066	.00060	.0017	5	
Ni	.0025	.00000	.0000	5	
Se	.2602	.02172	.0703	6	E
Ag	.1979	.00000	.0000	5	F
Tl	.0271	.00686	.0080	6	G
V	.0066	.00412	.0026	5	H
Zn	.0014	.00000	.0000	5	I
Ba	.0023	.00414	.0016	6	
Na	.0022	.00000	.0000	6	
K	.0081	.00000	.0000	6	

[1] Variance components were estimated by using the BMDP statistical software program 3V which employs a maximum likelihood approach to the estimation of the variance. To stabilize variance with respect to changes in the mean, a (natural) logarithmic transformation of the data was performed prior to application of the variance components analysis.

[2] "Error Variance" is variance between subsamples from the same aliquot.

[3] Estimated variance between aliquots within sludges.

(continued)

TABLE 1. (continued)

[4] Estimated standard error of the "Between Variance" estimate.

[5] A "Between Variance" value of 0.00000 indicates that the maximum likelihood estimate of the variance was negative and that the program adjusted it to the smallest possible value. Because of this adjustment, the formula for the standard error does not apply, and this is indicated by placing 0.000 in the "Standard Error" column. It is not intended to imply that the estimate is made without possible error.

[6] Each measurement was coded for data quality with 1 representing best quality. Each number given in the "Data Quality" column is the maximum of the code values given to the measurements of the corresponding element in its row. Precise meanings of each of the six code values is given elsewhere in this paper.

COMMENTS:

A - Two outliers on the left (-0.001 and 0.004) of data quality code 6 were removed from the set of eight measurements on the Fly Ash sludge. If these measurements were not removed, the three estimates in this row would be 0.2356, 0.02796 and 0.0614.

B - Large error variance is causd by the large variability of eight measurements from Industrial sludge. Prior to the log-transformation, one negative measurement from the Industrial Sludge was changed to the value of the minimum positive measurement (0.069) for As from that sludge.

C - Five 0.000 measurements on Mine Tailing Sludge changed to 0.001 prior to applying the log-transformation.

D - Measurements from Estuarine Sediment were not included because all measurements were negative.

E - Measurements from the Estuarine Sediment are not included because six of the eight measurements were negative. Prior to the log- transformation, three negative measurements from the River Sediment were changed to the value of the minimum positive measurement (0.046) for Se from that sludge.

F - Prior to the log-transformation, two negative measurements of the River Sediment were changed to the value of the minimum positive measurement (0.009) for Ag from that sludge. Large error variance is due to one large measurement (1.411, with the next highest measurement, 0.125), possibly a small nugget, in HW 1 sludge. It is unreasonable to abandon this measurement as it has quality code 1. However, without this measurement, the two variance estimates would have been 0.0428 and 0.00000.

(continued)

TABLE 1. (concluded)

G - Prior to the log-transformation, one negative measurement in Fly Ash sludge was changed to the value of the minimum positive measurement (0.077) for Tl in that sludge.

H - Prior to the log-transformation, two negative measurements on River Sediment were changed to the value of the minimum positive measurement (0.068) for V from that sludge.

I - One outlier (0.699) of data quality 5 was removed from the set of measurements on Mine Tailing Sludge where all other measurements were greater than 8 and of data quality 1.

TABLE 2. HOMOGENEITY STUDY SAMPLE STATISTICS FOR DIGESTS

(4g/200ml)

Element	Sludge	No. of Obs.	Data Quality[1]	Raw Data (mg/L) Mean	Raw Data (mg/L) Std. Dev.[3]	Log Data[2] Mean	Log Data[2] Std. Dev.[3]
Al	Fly Ash	8	1	243.702	17.187	5.494	0.072
	MineTailing	8	1	315.244	14.711	5.752	0.048
	Electro.	8	5	100.761	3.848	4.612	0.038
	Estuarine	8	1	308.309	51.312	5.718	0.176
	HW 1	8	1	131.488	4.472	4.878	0.035
	River	9	5	85.426	5.115	4.446	0.060
	Industrial	8	1	278.906	7.820	5.631	0.028
Sb	Fly Ash	8	6	0.042[4]	0.033[4]	-2.972	0.437
	Mine Tailing	8	3	0.242	0.029	-1.426	0.120
	Electro.	8	3	0.931	0.127	-0.081	0.148
	Estuarine	8	3	0.191	0.041	-1.679	0.232
	HW 1	8	3	0.285	0.027	-1.259	0.098
	River	9	3	0.511	0.196	-0.740	0.396
	Industrial	8	3	0.134	0.029	-2.028	0.220
As	Fly Ash	8	3	2.338	0.163	0.847	0.071
	Mine Tailing	8	5	12.242	0.286	2.505	0.023
	Electro.	8	3	1.261	0.043	0.231	0.034
	Estuarine	8	3	0.895	0.223	-0.139	0.259
	HW 1	8	3	0.991	0.174	-0.111	0.206
	River	9	3	2.055	0.295	0.710	0.154
	Industrial	8	6	0.310	0.294	-1.417	0.931
Be	Fly Ash	8	5	0.051	0.003	-2.983	0.063
	Mine Tailing	8	6	0.000	0.001	-6.908	0.000
	Electro.	8	3	0.003	0.000	-5.773	0.102
	Estuarine	8	3	0.013	0.001	-4.348	0.113
	HW 1	8	3	0.014	0.001	-4.306	0.040
	River	9	3	0.011	0.000	-4.491	0.038
	Industrial	8	3	0.005	0.000	-5.298	0.000

(continued)

TABLE 2. (continued)

Element	Sludge	No. of Obs.	Data Quality[1]	Raw Data (mg/L) Mean	Raw Data (mg/L) Std. Dev.[3]	Log Data[2] Mean	Log Data[2] Std. Dev.[3]
Cd	Fly Ash	8	3	0.030	0.006	-3.530	0.210
	Mine Tailing	8	3	0.044	0.006	-3.143	0.134
	Electro.	8	5	1.655	0.033	0.504	0.020
	Estuarine	8	6	-0.064	0.014	*	*
	HW 1	8	3	0.082	0.007	-2.500	0.088
	River	9	3	0.083	0.012	-2.499	0.157
	Industrial	8	3	0.401	0.013	-0.914	0.032
Ca	Fly Ash	8	5	84.112	1.432	4.432	0.017
	Mine Tailing	8	5	188.865	6.724	5.240	0.036
	Electro.	8	5	738.263	15.977	6.604	0.022
	Estuarine	8	1	73.927	4.511	4.301	0.062
	HW 1	8	4	1264.875	44.086	7.142	0.034
	River	9	5	435.220	12.407	6.075	0.029
	Industrial	8	4	1212.375	41.033	7.100	0.034
Cr	Fly Ash	8	5	0.469	0.041	-0.761	0.089
	Mine Tailing	8	3	0.090	0.014	-2.420	0.153
	Electro.	8	5	130.588	3.299	4.872	0.025
	Estuarine	8	5	0.733	0.074	-0.315	0.104
	HW 1	8	5	2.051	0.052	0.718	0.025
	River	9	4	503.200	18.491	6.220	0.037
	Industrial	8	5	1.045	0.025	0.043	0.024
Co	Fly Ash	8	3	0.195	0.018	-1.639	0.092
	Mine Tailing	8	3	0.165	0.039	-1.834	0.275
	Electro.	8	3	0.068	0.006	-2.695	0.090
	Estuarine	8	3	0.160	0.033	-1.853	0.232
	HW 1	8	3	0.177	0.009	-1.731	0.052
	River	9	6	0.024	0.016	-3.952	0.795
	Industrial	8	3	0.153	0.065	-1.982	0.311
Cu	Fly Ash	8	1	0.678	0.032	-0.390	0.048
	Mine Tailing	8	1	5.843	0.088	1.765	0.015
	Electro.	8	5	14.338	0.371	2.663	0.026
	Estuarine	8	1	0.372	0.016	-0.989	0.045
	HW 1	8	1	3.549	0.542	1.258	0.134
	River	9	5	2.100	0.077	0.741	0.036
	Industrial	8	1	5.902	0.165	1.775	0.028

(continued)

TABLE 2. (continued)

Element	Sludge	No. of Obs.	Data Quality[1]	Raw Data (mg/L) Mean	Raw Data (mg/L) Std. Dev.[3]	Log Data[2] Mean	Log Data[2] Std. Dev.[3]
Fe	Fly Ash	8	5	224.459	41.353	5.399	0.181
	Mine Tailing	8	5	190.285	7.664	5.248	0.041
	Electro.	8	5	486.688	7.877	6.188	0.016
	Estuarine	8	5	429.065	22.650	6.060	0.054
	HW 1	8	5	337.386	10.894	5.821	0.033
	River	9	4	1522.556	67.289	7.327	0.044
	Industrial	8	5	284.151	5.950	5.649	0.021
Pb	Fly Ash	8	3	0.207	0.043	-1.592	0.199
	Mine Tailing	8	5	101.140	0.932	4.616	0.009
	Electro.	8	5	17.135	0.373	2.841	0.022
	Estuarine	8	3	0.455	0.040	-0.790	0.086
	HW 1	8	5	3.628	0.164	1.288	0.045
	River	9	5	10.542	0.329	2.355	0.032
	Industrial	8	5	225.696	4.165	5.419	0.018
Mg	Fly Ash	8	5	14.143	0.773	2.648	0.056
	Mine Tailing	8	5	274.275	4.873	5.614	0.018
	Electro.	8	5	31.908	0.674	3.463	0.021
	Estuarine	8	5	137.178	5.878	4.920	0.043
	HW 1	8	5	428.836	8.543	6.061	0.020
	River	9	5	98.815	2.423	4.593	0.025
	Industrial	8	5	43.847	1.064	3.780	0.024
Mn	Fly Ash	8	5	0.885	0.058	-0.125	0.066
	Mine Tailing	8	4	1737.143	18.467	7.460	0.011
	Electro.	8	5	4.853	0.109	1.579	0.022
	Estuarine	8	5	4.220	0.190	1.439	0.046
	HW 1	8	5	6.838	0.106	1.922	0.016
	River	9	5	11.210	0.292	2.417	0.026
	Industrial	8	5	13.567	0.259	2.607	0.019
Mo	Fly Ash	8	5	0.527	0.021	-0.642	0.041
	Mine Tailing	8	5	1.307	0.031	0.267	0.024
	Electro.	8	5	0.277	0.009	-1.284	0.031
	Estuarine	8	5	0.059	0.009	-2.840	0.149
	HW 1	8	5	0.183	0.015	-1.704	0.080
	River	9	5	0.289	0.028	-1.246	0.098
	Industrial	8	5	0.098	0.008	-2.328	0.091

(continued)

TABLE 2. (continued)

Element	Sludge	No. of Obs.	Data Quality[1]	Raw Data (mg/L)		Log Data[2]	
				Mean	Std. Dev.[3]	Mean	Std. Dev.[3]
Ni	Fly Ash	8	3	0.433	0.040	-0.841	0.094
	Mine Tailing	8	3	0.353	0.017	-1.043	0.048
	Electro.	8	5	8.217	0.188	2.106	0.023
	Estuarine	8	3	0.427	0.022	-0.852	0.051
	HW 1	8	3	0.431	0.010	-0.841	0.023
	River	9	3	0.581	0.027	-0.544	0.046
	Industrial	8	5	2.969	0.056	1.088	0.019
Se	Fly Ash	8	5	0.259	0.069	-1.377	0.243
	Mine Tailing	8	5	0.515	0.061	-0.669	0.115
	Electro.	8	5	0.150	0.065	-2.070	0.769
	Estuarine	8	6	-0.045	0.073	*	*
	HW 1	8	5	0.407	0.092	-0.920	0.220
	River	9	6	0.080	0.175	-2.520	0.821
	Industrial	8	5	0.208	0.089	-1.661	0.480
Ag	Fly Ash	8	3	0.013	0.002	-4.360	0.131
	Mine Tailing	8	3	0.094	0.010	-2.371	0.105
	Electro.	8	3	0.126	0.005	-2.075	0.039
	Estuarine	8	5	0.025	0.005	-3.728	0.242
	HW 1	8	3	0.244[5]	0.477[5]	-2.268	1.129
	River	9	3	0.009	0.009	-4.432	0.211
	Industrial	8	3	0.190	0.006	-1.663	0.029
Tl	Fly Ash	8	6	0.091	0.060	-2.264	0.237
	Mine Tailing	8	3	1.507	0.316	0.395	0.181
	Electro.	8	3	0.394	0.037	-0.934	0.091
	Estuarine	8	6	0.164	0.042	-1.841	0.269
	HW 1	8	3	0.304	0.068	-1.215	0.230
	River	9	3	0.622	0.057	-0.478	0.092
	Industrial	8	3	0.414	0.028	-0.883	0.069
V	Fly Ash	8	5	1.511	0.066	0.412	0.044
	Mine Tailing	8	5	0.437	0.014	-0.828	0.031
	Electro.	8	5	0.381	0.006	-0.964	0.016
	Estuarine	8	5	0.833	0.075	-0.187	0.093
	HW 1	8	5	0.421	0.013	-0.865	0.030
	River	9	3	0.067	0.067	-2.401	0.228
	Industrial	8	5	0.275	0.009	-1.292	0.032

(continued)

TABLE 2. (continued)

Element	Sludge	No. of Obs.	Data Quality[1]	Raw Data (mg/L) Mean	Raw Data (mg/L) Std. Dev.[3]	Log Data[2] Mean	Log Data[2] Std. Dev.[3]
Zn	Fly Ash	8	1	1.076	0.072	0.071	0.068
	Mine Tailing	8	5	7.462[6]	2.736[6]	2.131	0.018
	Electro.	8	5	226.402	5.118	5.422	0.023
	Estuarine	8	1	2.146	0.104	0.763	0.048
	HW 1	8	1	3.538	0.101	1.263	0.028
	River	9	5	26.109	0.616	3.262	0.024
	Industrial	8	1	27.900	0.657	3.328	0.023
Ba	Fly Ash	8	5	12.541	0.198	2.529	0.016
	Mine Tailing	8	5	8.529	0.090	2.143	0.011
	Electro.	8	5	1.609	0.190	0.469	0.130
	Estuarine	8	5	0.693	0.080	-0.373	0.120
	HW 1	8	1	3.804	0.144	1.335	0.038
	River	8	6	0.985	0.029	-0.016	0.030
	Industrial	8	4	135.312	9.557	4.905	0.069
Na	Fly Ash	8	5	4.621	0.285	1.529	0.060
	Mine Tailing	8	5	61.020	2.522	4.110	0.041
	Electro.	8	5	1049.250	18.313	6.956	0.017
	Estuarine	8	5	171.790	2.824	5.146	0.016
	HW 1	8	5	4.750	0.354	1.556	0.073
	River	8	6	16.790	0.687	2.820	0.041
	Industrial	8	5	36.468	1.941	3.595	0.052
K	Fly Ash	8	5	31.494	2.705	3.446	0.088
	Mine Tailing	8	5	137.724	5.381	4.925	0.039
	Electro.	8	5	36.159	1.122	3.587	0.031
	Estuarine	8	5	64.315	6.926	4.158	0.111
	HW 1	8	5	16.306	1.641	2.787	0.102
	River	8	6	8.723	1.166	2.158	0.137
	Industrial	8	5	10.473	0.733	2.347	0.070

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[1] A data quality number in this column is the maximum of the data quality numbers for the individual measurements for an element in a sludge.

[2] The sample statistics are for data that have been corrected as stated in the comments in TABLE 1 and that are then logarithmically transformed. Hence in cases where outliers were removed, the number of observations used to obtain the sample means and standard deviations is not the same as that listed in the "No. of Obs." column.

(continued)

TABLE 2. (concluded)

[3] These two columns contain sample standard deviations of the measurements, or log-transformed measurements, of an element within a sludge.

[4] If the two outliers mentioned in comment A of Table 1 are removed, the sample mean and standard deviation of the remaining 6 measurements in Fly Ash sludge are 0.055 and 0.025, respectively.

[5] If the unusually large Ag measurement mentioned in comment F of Table 1 is removed from the data, the sample mean and standard deviation of the remaining 7 measurements in HW 1 sludge are 0.077 and 0.033, respectively.

[6] If the unusually small Zn measurement mentioned in Comment I of Table 1 is removed from the data, the sample mean and standard deviation of the remaining 7 measurements for Mine Tailing Sludge are 8.429 and 0.151, respectively.

APPENDIX D

METHOD 6010 INTERLABORATORY STUDY SAMPLE DESCRIPTION, PROCEDURES, AND SUPPLEMENTAL INSTRUCTIONS

Prepared by

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May 1986

FOREWORD

The University of Nevada, Environmental Research Center's Quality Assurance Laboratory has been tasked by the US EPA EMSL/LV to coordinate the ICP Method 6010 Study. This document describes the samples and solutions in this shipment. It also provides supplemental instructions meant to compliment those given in your SAS Task Directive. It is suggested that you read carefully both this document and the SAS Task Directive and resolve any questions you may have prior to beginning the study.

I. SAMPLES/SOLUTIONS DESCRIPTION

Table 1 summarizes the materials in this shipment. Please check them carefully.

TABLE 1

ITEM	UNITS SHIPPED	AMOUNT/BOTTLE	LABEL	DESCRIPTION/INSTRUCTIONS
1	4	50 mL	ICV#1 ICV#2 ICV#3 ICV#4	Initial calibration verification solutions. Do not dilute.
2	1	60 mL	X85	Interference check solution. Dilute 10 fold.
3	9	200 mL	G,H,I,J, K,L,M,N,O	Liquid Samples. Do not digest. Note, there are only 9 of these samples, not 10 as indicated by your Task Directive (Subtask 1).
4	7	16+ grams	T,U,V,W, X,Y,Z	Solid samples. To be digested. (Task Directive, Subtask 2)
5	2	50 mL	P,Q	Solid-sample spiking solutions.
6	2	100 mL	E,F	Coordinating laboratory QC solutions. To be digested as solid samples.

II. ITEM 1: Initial Calibration Verification Solutions, ICV#1, ICV#2, ICV#3, ICV#4.

A. Purpose. These solutions are provided to enable you to verify your calibration curves. True values are furnished by the coordinating laboratory, and the use of these solutions by the participating laboratory is required. A table of true values for the ICV solutions is given (see Attachment 1).

B. Analysis.
1. Do not dilute.
2. These solutions must be analyzed at least once immediately after calibration of the ICP.

Recalibration requires reanalysis of these solutions.

C. Reporting.

1. All sample data collected using the same calibration curve must be reported with the ICV results on FORM II. Report only those elements that are present in the ICV solutions as indicated on the Table of True Values (Attachment 1). Because cadmium, lead, silver, and thallium are in both ICV #1 and ICV #4, report the cadmium and lead values determined from the analysis of ICV Solution #1. For silver and thallium, report the analytical results from ICV Solution #4. YOU WILL HAVE TO PROVIDE YOUR OWN QC SOLUTION FOR THE VERIFICATION OF MOLYBDENUM. It is suggested that EPA Trace Metal Solution III, Concentration #2, WP 581, be used for this purpose.

III. ITEM 2: Interference Check Solution. ICS-X85

A. Purpose. This solution is provided to verify interelement interference corrections. This solution contains some, but not all of the major interferents one might find in a solid sample. Interferences caused by other analytes in high concentrations should be investigated by the participating laboratory as described in Method 6010 Section 3.

B. Analysis.

1. Dilute one-to-ten before analysis with a solution that is 2.5 percent (v/v) HCL and 5 percent (v/v) HNO_3.
2. Analyze at least once at the beginning and end of each analytical run and at least once every twenty samples as described in Method 6010 Section 7.6.3.
3. A Table of True Values for ICS-X85 is given in Attachment 1.

C. Reporting. Report the first and last ICS-X85 analytical results determined from the same analytical run on Form IV. Check the results for the ICS-X85 Solutions between the first and last (for problems) and rerun samples if necessary. Do not record the intermediate ICS-X85 results on any form, but include them with your raw data.

IV. ITEM 3: Liquid Samples G,H,I,J,K,L,M,N,O

A. Purpose. These digests were prepared by the coordinating lab so the results of the participating laboratories on identical samples can be compared.

Note only 9 solutions, not 10 as indicated in Subtask 1, are supplied.

B. Analysis.
   1. Do not digest these sample solutions.
   2. Analyze these solutions using method 6010 as modified for this SAS contract. The 1:4 dilution test is required and the method of standard additions (MSA) may be necessary. (See Section 7.6.5 of Method 6010).

C. Reporting.
   1. Results of each of these 9 samples should be reported individually in separate data packages.
   2. Fill out Form 1 in µg/L. These values must be interference corrected and may be the result of the method of standard additions. Do not report cyanide or percent solids for these liquid samples. For EPA sample I.D.,enter the alphabetic character from the sample label.
   3. Fill out Form II in µg/L. For initial calibration verification use the ICV#1, #2, #3, #4 results that were determined concurrently with this sample. (See Paragraph II above.) Give the name and source of the molybdenum initial calibration solution used at the bottom of Form II. For the continuing calibration, report the first continuing calibration set from raw data in the first column and report the last continuing calibration set in the second column of Form II. Check the results of the continuing calibration standards analyzed between the first and last set for values outside the ±10 percent control limits and rerun the samples if necessary. Do not record the intermediate continuing calibration results on any form, but they must be included with your raw data.
   4. Fill out Form III in units of µg/L. The initial calibration blank value should be determined by averaging the results of the first three standard blanks analyzed at the beginning of the analytical run as required in Method 6010 Section 7.6.1 and 7.6.1.2. Report 3 times the Standard Deviation (S.D.) value next to the mean in parentheses. For example, for three standard blanks with values of 10, 3, -2 µg/L, yielding a mean of 3.666 and a S.D. of 6.027, report as "4 (18)". For the continuing calibration blank values, columns 1-3, report the first three continuing calibration blank results; these will be the fourth, fifth, and sixth determinations of the blank standard in an analytical run. Report the result of the last

continuing calibration standard blank determined in the analytical run in the fourth column under continuing calibration. Do not report a preparation blank for samples G,H,I,J,K,L,M,N,O.

5. Fill out Form IV in μg/L. See the instructions for reporting ICS-X85 solution (see Paragraph III above).
6. Form V: Not required.
7. Form VI: Not required for samples G,H,I,J,K,L,M,N,O.
8. Fill out Form VII in μg/L. For instrument detection limits, report the values determined as outlined in the EPA Task Directive under Subtask 1. Do not report the lab control sample for liquid samples G,H,I,J,K,L,M,N,O.
9. Fill out Form VIII if the Method of Standard Additions was required. Use units of mg/L. Put the dilution of the zero addition in parenthesis on the left margin.
10. Fill out Form IX in g/L. If the first determination is overrange or above the linear calibration range, dilute the sample to the linear range to obtain the first value and then dilute 1:4 to check for physical interferences. A dilution scheme of 0, 1:4, 1:16, 1:64, is suggested. For initial concentration, the dilution factor should be entered in parentheses in the same column as the analytical result. For example, in a high-concentration sample where the undiluted and the 1:4 dilution were overrange, one might find a value of 87100 g/L in the 16-fold dilute sample. Report this as initial concentration 87100 (1:16). For this example, assuming no interferences, the "one-to-four" result would be reported as 21800 (1:64).
11. Form X: Not required.
12. Fill out Form XI in g/L.
13. Fill out Form XII in units of mg/L. If a correction factor is a quadratic $Ax^2 + Bx + C$, give only B in the format below.

	Al	Fe
Antimony:	-1.890/1000	-0.780/1000

That is, 1.890 mg/L of antimony is subtracted from the raw antimony result for every 1000 mg/L aluminum in the sample.

14. Fill out Form XIII in μg/L.

V. ITEM 4. Solid Samples T,U,V,W,X,Y,Z.

A. Purpose. These solid samples are to be digested according to Method 3050 (as described below and in the SAS contract), and analyzed using Method 6010.

B. Analysis.

1. Use Method 3050 with the modifications given below.

   a. Four grams of sample will be digested to 200 mL; therefore, reagent quantities designated in method 3050 must be doubled.

   b. An example of the digestion of the soil in Bottle T will serve to indicate these modifications of Method 3050. Take a 4-g aliquot and determine percent solids as per Method 3050 Paragraph 7.7. The soil used to determine percent solids WILL BE USED ALSO AS A DUPLICATE DIGESTION. DO NOT CONTAMINATE IT IN A DRYING OVEN. DO NOT THROW THE SAMPLE OUT ONCE PERCENT SOLIDS IS DETERMINED. Four 125 mL conical Phillips beakers are required. Weigh 4 grams ± 0.01g into each of three 125 mL conical Phillips beakers. Into the fourth beaker quantitatively tranfer the 4-g digest used to determine percent solids. THIS LATTER SOIL WILL BE DIGESTED AND REPORTED AS DUPLICATE NUMBER 2. Designate two of the other beakers as spike digestions. (Digest as many preparation blanks as necessary). The samples designated as spike aliquots will be spiked before digestion with 2 mL each of the solutions marked P and Q. Before digestion, add 2 mL from Solution P and 2 mL from Solution Q into SPIKE #1 and 2 mL of P and 2 mL of Q into SPIKE #2 (See Paragraph VI). Then begin the digestion procedure on all four aliquots as in Method 3050. Remember to double the amount of all reagents added during digestion because you are digesting 4 grams of sample to 200 mL (not 2 grams to 100 mL).

   c. At the same time a batch of solid samples are being digested, digest 50 mL of Solutions E and F in two separate beakers (see Paragraph VII below). These liquid samples should be diluted to 200 mL. For the analysis and reporting ignore the dilution; that is, report the analytical value of the diluted analyte. It is suggested that no more than two separate digestion batches be used in this study. Note also that only 100 mL of Solutions E and F (sufficient for two digestions) are provided. Solutions E and F represent the QC Solutions in the Task Directive (Subtask 2). The third QC sample described in the Task Directed Subtask 2 is not provided or required.

C. Reporting. Results of each of the solid samples T,U,V,W,X,Y,Z are to be reported as separate data packages as described below.
   1. Form I: Five of these forms will be filled out. Four of these forms are for reporting solid sample results. One of the forms is for reporting the results of sample Solutions E and F which were digested concurrently with the solid samples. All solid and sample solution values, must be interference corrected and may be the result of the method of standard additions. For solid samples, report values in mg/kg; i.e., all instrument values multiplied by 50. This is to correct for the dilution of the solid during digestion. Correct the final values for percent solids. For liquid samples E and F, report values in µg/L. Do not correct for Solution E and F 50 to 200 mL dilution during digestion when reporting the results. Report only silver, thallium, and manganese from Solution E and all other elements from Solution F. For example, the Solid Sample T report package will have five of Form 1 (DUP #1 T, DUP #2 T, SPIKE #1, SPIKE #2, Solution E-F). Check medium soil and N/A for cyanide on the form. Report percent solids as determined from DUP #2.
   2. Form II: Report as in liquid samples, (Paragraph IV, Section C.2 above).
   3. Form III: Report as indicated for liquid samples (Paragraph IV, C.2) instructions with the exception that the preparation blank results are given here.
   4. Form IV: Fill out in µg/L. (See Paragraph III, C Reporting instructions.)
   5. Form V: Not required.
   6. Form VI: Fill out in mg/kg of solid. Here the sample is DUP #1 and the duplicate is DUP #2. Do not fill out control limits.
   7. Form VII: Fill out in µg/L as indicated for liquid samples (Paragraph IV, C.8 above), with the exception that the Laboratory Control Sample column is filled out. The Laboratory Control Sample values are the results of analysis of your Laboratory Control Sample that was digested concurrently with this sample. While a Laboratory

Control Sample is not formally required by the contract, it is consistent with good laboratory practices. Give the name/source of the Solid Laboratory Control Sample used at the bottom of the form. Also note that these values may be the result of the method of standard addition.

8. Form VIII: Fill out in mg/L under concentration if the method of standard additions was required. Put the dilution of the zero addition in parenthesis on the left margin of the page.
9. Form IX: Fill out in g/L.
10. Form X: Not required.
11. Form XI: Fill out.
12. Form XII: Fill out as indicated for liquid samples (Paragraph IV, C.13, above.)
13. Form XIII: Fill out.

VI. ITEM 5. Solid Sample Spiking Solutions P and Q.

A. Purpose. These solutions will facilitate uniform soil spiking concentrations for the participant laboratories. This will allow statistical analysis of the interlaboratory precision and spike recovery. The true values of these solutions are not given.

B. Analysis.
1. Do not dilute.
2. Spike 2 mL of Spike Solution P and 2 mL of Spike Solution Q to each of the two 4-gram solid aliquots designated as spikes for each solid sample T,U,W,X,Y,Z. (See Paragraph V for instructions on solid digestions.)

C. Reporting: Solid sample spike recoveries are not calculated. Report the spiked solid samples on Form I as described in Paragraph V, C.1 reporting above.

VII. ITEM 6. Solutions E and F.

A. Purpose. Results from these solutions will allow interlaboratory statistical analysis of digestion precision. The results will also be used to evaluate the reliability of data from samples digested concurrently.

B. Analysis.
1. True values are not given.
2. Digest 50 mL of the Solutions E and F separately along with solid digestions. These solutions are to be digested as though they are solid samples. See solid samples (Paragraph V)) instructions. A sufficient quantity of solutions (100 mL each)

is provided for two digestion batches. During the digestion procedure the solutions will be diluted to 200 mL. This dilution is ignored during analysis and reporting.

C. Reporting: All solid samples digested concurrently with Solutions E and F should be reported with the results of Solution E and F reported on Form I. Report only silver, thallium and manganese from Solution E and all other elements from solution F using units of g/L.

VIII. General Reporting.

Values greater than the detection limit but less than 10 times the detection limit should be reported in brackets. When reporting the analytical values for solid samples, multiply the detection limit in mg/L by 50 to obtain the mg/kg detection limit. Legible photo copies of all raw data, with keys to sample names, must be submitted as part of the data package to the coordinating lab. (Address given below).

We invite your comments in writing pertaining to any part of the study or the methods.

MAILING ADDRESS:

Quality Assurance Laboratory
University of Nevada, Las Vegas
4505 S. Maryland Parkway
Las Vegas, Nevada 89154
Telephone (702) 739-3142

If there are any questions, ask for:

Clifton Jones
Donald Schoengold
Joseph Campana, Director

NOTE: All solutions and digestions not used during analysis MUST BE RETURNED TO THE COORDINATING LABORATORY. The solutions to be returned include:

		Number of bottles
1.	Liquid samples G,H,I,J,K,L,M,N,O (Item 3)	7
2.	Solid samples and SOIL DIGESTIONS T,U,V,W,X,Y,Z (Item 5).	7 solid and 28 digests
3.	Solid spiking solutions P and Q (Item 5).	2
4.	Liquid samples E and F (Item 6).	2

For Courier Delivery Service use the following address:

University of Nevada, Las Vegas
Quality Assurance Laboratory
Museum Bldg., Rm. 160
Las Vegas, Nevada 89109

For any other questions regarding shipping, please contact Carol Moore at (702) 739-3142.

INITIAL CALIBRATION VERIFICATION SOLUTIONS

Four Initial Calibration Verification solutions (ICV's) have been prepared to check initial calibration curves. These solutions do not require dilution.

ICV-1:

(Undiluted)

Element	Value (ug/L)
Al	1910
Ba	1740
Be	435
Cd	451
Cr	447
Ca	9220
Co	439
Cu	348
Fe	1330
Pb	9130
Mg	8560
Mn	402
K	46380
Ni	432
Na	46900
Ag	-400 use ICV #4 results
V	619
Zn	2630

ICV-2: (Undiluted)

Element	Value (ug/L)
As	818
Se	1728

ICV-3: (Undiluted)

Element	Value (ug/L)
Sb	8700

ICV-4: (Undiluted)

Element	Value (ug/L)
Pb	~1000 use ICV #1 results
Cd	~1000 use ICV #1 results
Tl	950
Ag	970

INTERFERENCE CHECK SAMPLE

ICS X-85

The Interference Check Sample, ICS X-85, is a concentrate that is intended to be used to check the proper operation of an Inductively-Coupled Plasma Spectrometer.

The concentrations of the elements contained are given in Table 1.

The concentrate as supplied should be diluted 1:10 with 2-2.5% nitric acid (V/V). The dilution should be performed by measuring 1 volume of the concentrate into a calibrated glass volumetric flask. The final volume should then be adjusted to 10 volumes. (Because of the high salt content of the concentrate, addition of 9 volumes of acid to one volume of the concentrate will not necessarily produce a total of 10 volumes.)

The ICS concentrate is composed of nitrate salts. A very small amount of perchlorate is present, but it is so small that it can be ignored.

The ICS concentrate is stable at room temperature, but should not be refrigerated. If there is any indication that the material has been frozen, it should be discarded. To insure the stability of the silver contained in the ICS, the concentrate should be stored in a dark cabinet.

This material was prepared by the University of Nevada, Las Vegas, Quality Assurance Laboratory. The accepted concentrations are based on the data from five independent laboratories. If there is any question about the samples, please call (702) 739-3142.

TABLE 1

Concentrations for X-85

ELEMENT	Concentration (ug/L)
Ag	986
Ba	472
Be	456
Cd	964
Cr	985
Co	478
Cu	509
Mn	522
Ni	913
Tl	1090
V	471
Zn	948
Pb	4630
Al	503000
Ca	499000
Fe	198000
Mg	497000

Date ___________

COVER PAGE
INORGANIC ANALYSES DATA PACKAGE

Lab Name ____________________ Case No. ____________________

SOW No. ____________________ Q.C. Report No. ____________

Lab Receipt Date ____________

Sample Numbers

EPA No.	Lab ID No.	EPA No.	Lab ID No.

Comments: ____

ICP interelement and background corrections applied? Yes ___ No ___.

If yes, corrections applied before _____ or after _____ generation of raw data.

Footnotes:

NR - Not required by contract at this time
Form 1:
Value - If the result is a value greater than or equal to the instrument detecion limit but less than the contract-required detection limit, report the value in brackets (i.e., [10]). Indicate the analytical method used with P (for ICP), A (for Flame AA) or F (for Furnace AA).
U - Indicates element was analyzed for but not detected. Report with the instrument detection limit value (e.g., 10U).
E - Indicates a value estimated or not reported due to the presence of interference. Explanatory note included on cover page.
S - Indicates value determined by Method of Standard Addition.
N - Indicates spike sample recovery is not within control limits.
* - Indicates duplicate analysis is not within control limits.
+ - Indicates the correlation coefficient for method of standard addition is less than 0.995
M - Indicates duplicate injection results exceeded control limits.

Indicate method used: P for ICP; A for Flame AA and F for Furnace.

Form I

EPA Sample No.

Date __________

INORGANIC ANALYSIS DATA SHEET

LAB NAME __________ CASE NO. __________

SOW NO. __________

LAB SAMPLE ID. NO. __________ QC REPORT NO. __________

Elements Identified and Measured

Concentration: Low ______ Medium ______

Matrix: Water ______ Soil ______ Sludge ______ Other ______

ug/L or mg/kg dry weight (Circle One)

1. Aluminum __________
2. Antimony __________
3. Arsenic __________
4. Barium __________
5. Beryllium __________
6. Cadmium __________
7. Calcium __________
8. Chromium __________
9. Cobalt __________
10. Copper __________
11. Iron __________
12. Lead __________

Cyanide __________

13. Magnesium __________
14. Manganese __________
15. Molybdenum __________
16. Nickel __________
17. Potassium __________
18. Selenium __________
19. Silver __________
20. Sodium __________
21. Thallium __________
22. Vanadium __________
23. Zinc __________

Precent Solids (%) __________

Footnotes: For reporting results to EPA, standard result qualifiers are used as defined on Cover Page. Additional flags or footnotes explaining results are encouraged. Definition of such flags must be explicit and contained on Cover Page, however.

Comments: __________

Lab Manager __________

Form II

Q. C. Report No. ________

INITIAL AND CONTINUING CALIBRATION VERIFICATION[3]

LAB NAME ____________________

CASE NO. ____________________

SOW NO. ____________________

DATE ____________________

UNITS ____________________

Compound	Initial Calib.[1]			Continuing Calibration[2]					
Metals:	True Value	Found	%R	True Value	Found	%R	Found	%R	Method[4]
1. Aluminum									
2. Antimony									
3. Arsenic									
4. Barium									
5. Beryllium									
6. Cadmium									
7. Calcium									
8. Chromium									
9. Cobalt									
10. Copper									
11. Iron									
12. Lead									
13. Magnesium									
14. Manganese									
15. Molybdenum									
16. Nickel									
17. Potassium									
18. Selenium									
19. Silver									
20. Sodium									
21. Thallium									
22. Vanadium									
23. Zinc									
Other: ________									
________									
Cyanide									

Initial Calibration Source____________ [2] Continuing Calibration Source____________

[3] Control Limits: Mercury and Tin 80-120; Other Metals 90-110; Cyanide 85-115

[4] Indicate Analytical Method Used: P - ICP; A - Flame AA; F - Furnace AA

Form XIII (Quarterly)
ICP Linear Ranges

LAB NAME ______________________________ ICP Model Number ________________

DATE ______________________________

Analyte	Integration Time (Seconds)	Concentration (ug/L)	Analyte	Integration Time (Seconds)	Concentration (ug/L)
1. Aluminum			13. Magnesium		
2. Antimony			14. Manganese		
3. Arsenic			15. Molybdenum		
4. Barium			16. Nickel		
5. Beryllium			17. Potassium		
6. Cadmium			18. Selenium		
7. Calcium			19. Silver		
8. Chromium			20. Sodium		
9. Cobalt			21. Thallium		
10. Copper			22. Vanadium		
11. Iron			23. Zinc		
12. Lead					

Footnotes: • Indicate elements not analyzed by ICP with the notation "NA".

COMMENTS: ____

____

____

____

Lab Manager ____________________

Form XII (Quarterly) (cont'd)

ICP Interelement Correction Factors

LABORATORY________________________ ICP Model Number______________

DATE ________________

		Interelement Correction Factors for							
Analyte	Analyte Wavelength (nm)								
1. Antimony									
2. Arsenic									
3. Barium									
4. Beryllium									
5. Cadmium									
6. Chromium									
7. Cobalt									
8. Copper									
9. Lead									
10. Manganese									
11. Molybdenum									
12. Nickel									
13. Potassium									
14. Selenium									
15. Silver									
16. Sodium									
17. Thallium									
18. Vanadium									
19. Zinc									

COMMENTS:____

Lab Manager____________________

Form XII (Quarterly)

ICP Interelement Correction Factors

LABORATORY______________________________ ICP Model Number________________

DATE ________________________

		Interelement Correction Factors for							
Analyte	**Analyte Wavelength (nm)**	**Al**	**Ca**	**Fe**	**Mg**				
1. Antimony									
2. Arsenic									
3. Barium									
4. Beryllium									
5. Cadmium									
6. Chromium									
7. Cobalt									
8. Copper									
9. Lead									
10. Manganese									
11. Molybdenum									
12. Nickel									
13. Potassium									
14. Selenium									
15. Silver									
16. Sodium									
17. Thallium									
18. Vanadium									
19. Zinc									

COMMENTS:____

____

Lab Manager______________________________

Form IX

Q. C. Report No. ______

ICP SERIAL DILUTIONS

LAB NAME ____________________

CASE NO. ____________

EPA Sample No. __________

DATE ____________________

Lab Sample ID No. ________

Units ____________

Matrix ____________

Compound	Initial Sample Concentration(I)	Serial Dilution Result(S)[1]	% Difference[2]
Metals: 1. Aluminum			
2. Antimony			
3. Arsenic			
4. Barium			
5. Beryllium			
6. Cadmium			
7. Calcium			
8. Chromium			
9. Cobalt			
10. Copper			
11. Iron			
12. Lead			
13. Magnesium			
14. Manganese			
15. Nickel			
16. Potassium			
17. Selenium			
18. Silver			
19. Sodium			
20. Thallium			
21. Vanadium			
22. Zinc			
Other: Molybdenum			

[1] Diluted sample concentration corrected for 1:4 dilution (see Exhibit D)

[2] Percent Difference = $\frac{|I - S|}{I} \times 100$

NR - Not Required, initial sample concentration less than 10 times IDL

NA - Not Applicable, analyte not determined by ICP

Form VIII

Q.C. Report No. ________

STANDARD ADDITION RESULTS

LAB NAME ______________________ CASE NO. ______________

DATE __________________________ UNITS ______________

EPA		0 ADD	1 ADD		2 ADD		3 ADD		FINAL	
Sample #	Element	ABS.	CON.	ABS[1]	CON.	ABS.[1]	CON.	ABS.[1]	CON.[2]	r*

[1] CON is the concentration added, ABS. is the instrument readout in absorbance or concentration.

[2] Concentration as determined by MSA

*"r" is the correlation coefficient.

+ - correlation coefficient is outside of control window of 0.995.

Form VI

Q. C. Report No. ______

DUPLICATES

LAB NAME ____________________

DATE ____________________

CASE NO. ____________________

EPA Sample No. ______________

Lab Sample ID No. ___________

Units ____________________

Matrix ______________

Compound	Control Limit[1]	Sample(S)	Duplicate(D)	RPD[2]
Metals: 1. Aluminum				
2. Antimony				
3. Arsenic				
4. Barium				
5. Beryllium				
6. Cadmium				
7. Calcium				
8. Chromium				
9. Cobalt				
10. Copper				
11. Iron				
12. Lead				
13. Magnesium				
14. Manganese				
15. Molybdenum				
16. Nickel				
17. Potassium				
18. Selenium				
19. Silver				
20. Sodium				
21. Thallium				
22. Vanadium				
23. Zinc				
Other: ________				
Cyanide				

* Out of Control

[1] To be added at a later date.

[2] $RPD = [|S - D|/((S + D)/2)] \times 100$

NC - Non calculable RPD due to value(s) less than CRDL

Form V

Q. C. Report No. ______

SPIKE SAMPLE RECOVERY

LAB NAME ____________________

DATE ____________________

CASE NO. ____________
EPA Sample No. ____________
Lab Sample ID No. ____________
Units ____________

Matrix ____________

Compound	Control Limit %R	Spiked Sample Result (SSR)	Sample Result (SR)	Spiked Added (SA)	%R[1]
Metals:					
1. Aluminum	75-125				
2. Antimony	"				
3. Arsenic	"				
4. Barium	"				
5. Beryllium	"				
6. Cadmium	"				
7. Calcium	"				
8. Chromium	"				
9. Cobalt	"				
10. Copper	"				
11. Iron	"				
12. Lead	"				
13. Magnesium	"				
14. Manganese	"				
15. Molybdenum	"				
16. Nickel	"				
17. Potassium	"				
18. Selenium	"				
19. Silver	"				
20. Sodium	"				
21. Thallium	"				
22. Vanadium	"				
23. Zinc	"				
Other: ______					
Cyanide	"				

[1] %R = [(SSR - SR)/SA] x 100

"N" - out of control

"NR" - Not required

Comments: ____

Form IV

Q. C. Report No. ________

ICP INTERFERENCE CHECK SAMPLE

LAB NAME ____________________

CASE NO. ____________________

Check Sample I.D. ____________

DATE ____________________

Check Sample Source ____________

Units ____________________

Compound	Control Limits[1]		True[2]	Initial		Final	
	Mean	Std. Dev.		Observed	%R	Observed	%R
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Molybdenum							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other: ________							

[1] Mean value based on n = ______.

[2] True value of EPA ICP Interference Check Sample or contractor standard.

Form III

Q. C. Report No. ______

BLANKS

LAB NAME ____________________

DATE ____________________

Matrix ______________

CASE NO. ____________________

UNITS ____________________

Compound	Initial Calibration Blank Value	Continuing Calibration Blank Value 1	2	3	4	Preparation Blank Matrix: ______ 1	Matrix: ______ 2
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Molybdenum							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other:							
Cyanide							

APPENDIX E

(Note-All attachments referred to in this appendix can be found in other appendices to this report.)

PARTICIPATING LABORATORIES STATEMENT-OF-WORK

TASK: Participating Laboratories for ICP Method 6010 Study

REQUESTOR: Thomas A. Hinners
Environmental Monitoring Systems Laboratory
Quality Assurance Laboratory
Las Vegas, Nevada 89114
Telephone: FTS 545-2140, COML (702) 798-2140

GOAL: To determine the precision, accuracy and scope of ICP Method 6010 when applied to sludge-type wastes

Each participating laboratory will conduct analyses by inductively coupled plasma optical emission spectroscopy (ICP) for the 23 elements specified in the attached version of sludge digestion method 3050 according to instructions in Method 6010 for the following:

Subtask 1: 10 solutions requiring no digestion

ICP analysis will involve the wavelengths listed for the elements in Method 6010, or alternate wavelengths that satisfy the detection limits specified on the modified CLP Form XI (attached). Report the wavelengths and CLP instrumental detection limits (IDLs) on modified CLP Form XI (attached). Note that ICP (not AA) IDL values are required for all elements including arsenic and selenium. Boron and silicon are excluded from the elements listed in Method 3050 because the digestion procedure in Method 3050 is not adequate for dissolving refractory compounds of these elements. Although molybdenum is not on the CLP element listing, it is included in Method 6010, Method 3050, and (in place of mercury) on the modified CLP Form XI. If the concentration of any required element in these solutions exceeds the calibrated range, repeatedly dilute [with a solution that has 2.5% (v/v) HCl and 5% (v/v) HNO_3] and analyze portions of those digests until all 23 elements have been measured in the calibrated range.

Both simultaneous and sequential instruments are desired in the study. To provide a uniform measurement basis for each version of instrument, measurements with simultaneous instruments (and sequentials that record at a point per element) will be obtained from three 10-second integrations while 1-second steps will be used for sequential instruments that scan peaks for quantification.

Before any field samples are analyzed under this contract, the instrumental detection limits (IDLs) must be determined within 30 days of the start of the analyses and must meet the levels specified on revised CLP Form XI. The instrumental detection limits (in ug/L) shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution at a concentration 3-5 times the expected IDL, with 7 consecutive measurements per day.

Test for the need to use the method of standard additions (as mandated in Section 7.6.5 of Method 6010) by diluting solutions 1:4 (i.e., 1 part sample plus 3 parts solvent) with a solvent consisting of 2.5% (v/v) HCl and 5% (v/v) HNO_3. If the concentration of an element in these diluted solutions is at least 10 times the participating laboratory's CLP instrumental detection limit (IDL) and multiplication of the diluted concentration by 4 does not produce a value that is within 10% of the concentration obtained on the undiluted digest, apply the method of standard additions (MSA) for that element using (where feasible) the undiluted digest. Report the dilution test results on revised Form IX (attached). For element concentrations that are measurable but too low for this dilution test, spike a portion of the undiluted digest to produce a concentration that is 20 times the laboratory's IDLs while keeping dilution of the digest to a minimum. If the expected and observed concentrations for the spiked digest differ by more than 10%, apply the method of standard additions for determining that element in that waste. MSA is not required when an element concentration is undetected in an undiluted digest or a spike added to a digest is precipitated. Flag latter data with "pcp" (for precipitate) on Form I.

If the method of additions is used for determining the concentration of an element in a digest, the following conditions apply:

a. data must be obtained that is in the linear calibration range,

b. the digest must be analyzed unspiked and at three spike levels (with the unspiked portion diluted to the same extent as the spiked portions but no more than 5%) designed to increase the apparent digest concentration by 1x, 2x and 4x (but not beyond the linear range) and no less than 1x IDL, 2x IDL, and 4x IDL,

c. the data will be subjected to least squares (linear regression) analysis to obtain the MSA concentration (i.e., the intercept), the slope, and the correlation coefficient; and the results reported on CLP Form VIII and the concentration flagged on CLP Form I with the letter "s" (to signify determination by standard additions),

d. if the correlation coefficient (r) for an MSA analysis is less than 0.995, flag the data on CLP Form I with the symbol "+".

Subtask 2: Seven solid wastes, 3 QC solutions and a blank to be digested according to the procedure in the attached version of Method 3050.

Each laboratory will receive 16-gram portions of the 7 solid wastes to be used as follows:

1. weigh four 4-gram portions of each waste (to the nearest 0.01 g) into 4 acid-cleaned beakers. Record the gross weight for one of the beakers with the portion to be dried to determine the solids content (per Method 3050). Total weighings for this subsampling are 4 x 7 wastes = 28. Although Method 3050 allows 1-to 2-gram portions for each 100 ml of digest, use of the higher proportion is specified here to provide an evaluation of the method at the maximum dissolved-solids level.

2. for each waste, add spiking solution (in the volumes to be specified by the coordinating laboratory) to the sample aliquots in two of these beakers. Total predigestion spiking is 2 x 7 wastes = 14.

3. for each waste determine the percent solids on one of the weighed (unspiked) portions following the procedure in the attached version of Method 3050. Total solids determinations are 7 (1 per waste). Digest these dried portions along with the other 3 portions per step 4 below.

4. digest the 2 spiked and the 2 unspiked portions of each waste plus a QC solution (provided) and a blank according to the procedure for ICP analysis in the attached version of Method 3050. Note that Step 7.6 in Method 3050 is to be excluded because it is not specified for ICP analyses. Since Method 3050 describes the digestion procedure when 2-grams of sample are used to produce 100 ml of digest, twice the reagent volumes specified in sections 7.2-7.5 in Method 3050 need to be used to yield 200-ml digests from the 4-gram portions specified for this study in step 1 above. Store the resultant 200-ml digests in acid-cleaned plastic bottles, and conduct ICP analyses (as for Subtask 1) within 7 days for the 23 elements listed in the attached version of Method 3050. If the concentration of any required element in these digests exceeds the calibrated range, repeatedly dilute [with a solution that has 2.5% (v/v) HCl and 5% (v/v) HNO_3] and analyze portions of those digests until all 23 elements have been measured in the calibrated ranges. Report results on the CLP Cover Page and on revised Forms I, V, and VI. Total digestions are 32 (4 x 7 wastes + 3QC + Blank).

Use revised Forms II and III to report initial and continuing calibration data, revised Form IV to report results for ICP Interference Check Sample, revised Form XII to report Interelement Correction Factors, and revised Form XIII to report ICP Linear Ranges. Provide raw data package as for CLP.

Ship the unused portions of all solutions (including the 28 digests prepared at the participating laboratory) to the following address using second-day delivery via Federal Express against 3rd party account number xxyxxxxxxx.

APPENDIX F
COORDINATING LABORATORY STATEMENT-OF-WORK

(Note-All attachments referred to in this appendix can be found in other appendices to this report.)

TASK: Coordinating Laboratory for ICP Method 6010 Study

REQUESTOR: Thomas A. Hinners
Environmental Monitoring Systems Laboratory
Quality Assurance Laboratory
Las Vegas, Nevada 89114
Telephone: FTS 545-2140, COML (702) 798-2140

The coordinating laboratory will aliquot, digest, analyze, spike, and distribute wastes and digests to the participating laboratories in the ICP Method 6010 study. The participating laboratories will also receive spiking solutions and blind quality control solutions from the coordinating laboratory. The results from the participating laboratories will be summarized with a statistical evaluation by the coordinating laboratory.

The coordinating laboratory will perform the following:

1. Obtain 350-gram portions of 4 homogenized sludge-type wastes (drying solids, an electoplating waste, QC soil 1 from EMSL-LV and the UNLV mine waste) plus river sediment (SRM 1645), estaurine sediment (SRM 1646) and coal fly ash (SRM 1633a) by purchase from NBS, and produce 13 x 20-gram aliquots of each material in acid-cleaned plastic bottles (13 x 7 wastes = 91 aliquots in total). After subsampling from some of these aliquots, they will be sent to the participating laboratories in the ICP Method 6010 study. Any portions remaining at the end of the project will be sent to the Task Monitor. Sample consumption: 260g in aliquots (13 x 20g), 40g for bulk digestion (paragraph #4), 50g spare portion.

2. To assess homogeneity of the endogeneous element concentrations, remove 2-gram portions (for each 100 ml of digest needed) randomly from 7 of the aliquots for each waste and digest these portions separately according to the procedure (for ICP analysis) in the attached version of Method 3050. Note that step 7.6 in Method 3050 is to be excluded because it is not specified for ICP analyses. Total digests for this section are 49 (7 per waste x 7 wastes). The digests of the NBS materials will provide an assessment of the efficiency and repeatability of the digestion procedure for those element concentrations certified by NBS. Although Method 3050 allows 1-to 2-gram portions for each 100 ml of digest, use of the upper weight is specified here to provide an evaluation of the method at the maximum solid-to-liquid ratio.

3. Remove a portion from each of these digests and conduct one ICP analysis (without conducting MSA tests or MSA) on each such that every specified element is measured in at least 6 of the digests for each waste material for the 23 elements specified in the attached version of Method 3050. Data for each element on at least 6 digests per waste can be obtained with 7 digests by excluding a different 3 elements from each digest analysis. If the concentration of any required element in the digests

exceeds the calibrated range, repeatedly dilute [with a solution that has 2.5% (v/v) HCl and 5% (v/v) HNO_3] and analyze portions of those digests until all elements have been measured in the calibrated range.

ICP analysis will involve the wavelengths listed for the elements in Method 6010, or alternate wavelengths that satisfy the detection limits specified on revised CLP Form XI (attached). Report the wavelengths selected and the CLP instrumental detection limits (IDLs) on revised CLP Form XI. Note that ICP (not AA) IDL values are required for all elements including arsenic and selenium. Boron and silicon are excluded from the elements listed in Method 3050 because the digestion procedure in Method 3050 is not adequate for dissolving refractory compounds of these elements. Although molybdenum is not on the CLP element listing, it is included in Method 6010, Method 3050, and (in place of mercury) on revised CLP Form XI.

Both simultaneous and sequential instruments are desired in the study. To provide a uniform measurement basis for each version of instrument, measurements with simultaneous instruments (and sequentials that record at a point per element) will be obtained from three 10-second integrations while 1-second steps will be used for sequential instruments that scan peaks for quantification.

Before any field samples are analyzed under this contract, the instrumental detection limits (IDLs) must be determined within 30 days of the start of the analyses and must meet the levels specified on revised CLP Form XI. The instrumental detection limits (in ug/L) shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution at a concentration 3-5 times the expected IDL, with 7 consecutive measurements per day.

4. Conduct a larger-scale digestion of 40 grams of each waste material (proportional to 2g of waste to 100 ml of final digest) to produce a volume of at least 2.0 liters. Participating laboratories need to receive sufficient volume of each composite digest to allow for a direct analysis and MSA testing plus the potential for 3 spike levels (if the method of standard additions is needed) as well as any reanalyses when QC check solutions are not within acceptance limits. At least 1500 ml would be required in order to provide 100 ml to 5 labs with simultaneous instruments and 200 ml to 5 labs with sequential instruments.

5. Spike the undiluted bulk digests (1 per waste) to provide 2.0 liters that has all 23 elements (specified in Method 3050) present at no less than 100 times the coordinating laboratories CLP instumental detection limits (when consistent with solubilities) while diluting each digest less than 5% (so that the matrix concentrations are not altered significantly). One source of standards for the spiking are the SRM 2121-2129 spectrometric solutions from NBS with single-element concentrations at 10,000 mg/l. After the digests are spiked and mixed, store these solutions at room temperature for at least 48 hours. If precipitation or turbidity is observed in a spiked solution, the solution will be clarified by centrifugation or filtration.

6. Prepare 1000 ml of at least one (and not more than 3) quality control (QC) solutions for the 23 elements with concentrations such that 1 + 3 dilution will yield values near the middle of the linear calibration ranges. These solutions will be used to evaluate the calibration uniformity and digestion recoveries of the laboratories participating in the Method 6010 evaluation study. Incompatibility of the standards or interference interests may make more than one QC solution necessary.

7. Analyze by ICP for the 23 specified elements in the 7 spiked digests (from paragraph #5 above) and all QC solutions (from paragraph #6 above) at 4 ± 2 days, 2 weeks ± 2 days and 6 weeks ± 2 days following preparation to monitor stability of the element concentrations. Tests for the need for the method of standard additions (MSA) and apply MSA (where needed) on the 2-week and 6-week analyses following the procedure below. Based on results from the 2-week MSA tests, conduct MSA where appropriate on the 6-week analyses.

Test for the need to use the method of standard additions (as mandated in Section 7.6.5 of Method 6010) by diluting solutions 1:4 (i.e., 1 part sample plus 3 parts solvent) with a solvent consisting of 2.5% (v/v) HCl and 5% (v/v) HNO_3. If the concentration of an element in these diluted solutions is at least 10 times the participating laboratory's CLP instrumental detection limit (IDL) and multiplication of the diluted concentration by 4 does not produce a value that is within 10% of the concentration obtained on the undiluted digest, apply the method of standard additions (MSA) for that element using (where feasible) the undiluted digest. Report the dilution test results on Form IX (attached). For element concentrations that are measurable but too low for this dilution test, spike a portion of the undiluted digest to produce a concentration that is 20 times the laboratory's IDLs (or below any expected solubility limits) while keeping dilution of the digest to a minimum. If the expected and observed concentrations for the spiked digest differ by more than 10%, apply the method of standard additions for determining that element in that waste. MSA is not required when an element concentration is undetected in an undiluted digest or a spike added to a digest is precipitated. Flag latter data with "pcp" on Form I.

If the method of additions is used for determining the concentration of an element in a digest, the following conditions apply:

a. data must be obtained that is in the linear calibration range,

b. the digest must be analyzed unspiked and at three spike levels (with the unspiked portion diluted to the same extent as the spiked portions but no more than 5%) designed to increase the apparent digest concentration by 1x, 2x and 4x (but not beyond the linear range) and no less than 1x IDL, 2x IDL, and 4x IDL,

c. the data will be subjected to least squares (linear regression) analysis to obtain the MSA concentration (i.e., the intercept), the slope, and the correlation coefficient; and the results reported on CLP Form

VIII and the concentration flagged on CLP Form I with the letter "s" to signify determination by standard additions,

d. if the correlation coefficient (r) for an MSA analysis is less than 0.995, flag the data on CLP Form I with the symbol "+".

8. Remove 2-g portions (for each 100 ml of digest needed) from two of the aliquot bottles (para #1), not subsampled for the homogeneity evaluation (para #2), for each waste and spike the separate portions with mixed standard solutions such that the resultant digests will be expected to have concentrations for all 23 elements that are at least 100 times the coordinating laboratory's CLP instrumental detection limits. Spiking solutions will also be sent to the participating laboratories to allow for spiking of 2 portions of each waste. Conduct ICP analyses on each spiked waste after following the digestion procedure in Method 3050. Test these digests to determine the need for MSA (as specified above in section #3) and, if necessary, conduct MSA analyses.

9. Determine the solids content of each waste material in duplicate using a 2-g portion from 2 aliquot bottles (para #1), select bottles not subsampled for either homogeneity testing (para #3) or spiking (para #8), following the procedure in Method 3050. Method 3050 specifies that element concentrations will be reported on a dry-weight basis.

10. After the 4th-day measurements specified in paragraph #7 have been made, send in acid-cleaned bottles the following to the laboratories participating in the Method 6010 evaluation at the addresses provided by Rock Mangeon (telephone 703-683-0885 or FTS 8-557-2490):

a. 200-ml portions of the spiked digests (para #5) to as many as 5 labs with sequential instruments,

b. 100-ml portions of the spiked digests (para #5) to as many as 5 labs with simultaneous instruments,

c. one aliquot of each waste (para #1) containing at least 16g,

d. 100 ml of each of 3 QC solutions (para #6) for sequential-instrument labs and 50 ml for simultaneous-instrument labs to be analyzed by participant labs both with and without digestion. For sequential instruments 50 ml will be digested to yield 200 ml of digest and for simultaneous instruments 25 ml will be digested to yield 50 ml of digest. Portions for analysis without digestion will simply be subjected to 1 + 3 dilution with a solution containing 2.5% HCl and 5% HNO_3 before analysis,

e. spiking solutions and spiking instructions for portions of each waste subsampled in duplicate by participant labs (using 2g for each 100 ml of digest needed) digest needed) such that the resultant digests will be expected to have concentrations for all 23 elements that are at least 100 times the coordinating laboratory's

CLP instrumental detection limits.

By having each participating laboratory add the spiking solution after the portions are removed, the potential for non-homogeneous spiking of the solid materials in bulk is avoided as is this source of variability for results from the laboratories. If the coordinating laboratory spiked portions for the participating laboratories, the evaluation would not reflect the aliquotting and weighing by each lab that are parts of Method 3050 in preparation for measurements by Method 6010. The requirement that the participating labs provide raw data information will permit verification of the spiked waste data received from the participants. [Participants could not just analyze spiking solutions separately and add values to those for the unspiked digests because the raw data would be missing for the spiked wastes.]

11. Report element concentrations (on a dry-weight basis) using CLP forms as appropriate and provide copies of instrument printouts for all analyses as well as the results for the solids determinations to the Task Monitor.

12. Provide advise to the participating laboratories and (if necessary) send replacement digests, waste aliquots, QC solutions and spiking solutions.

13. Prepare a report that tabulates the results from the participating laboratories and provides a statistical evaluation.

APPENDIX G

Participating Laboratories Data Package Audit Reports

The two attachments are audit reports (edited) of the participating laboratories' Method 6010 data packages. The first audit was to ensure that each data package contained all the required deliverables. The second audit included computer-aided checks of all QA/QC parameters to assure that all requirements such as the application of the method of standard additions were satisfied. The paritícpating laboratories are coded in the attachments.

Attachment 1

QUALITY ASSURANCE LABORATORY
ENVIRONMENTAL RESEARCH CENTER

UNIVERSITY OF NEVADA, LAS VEGAS
4505 MARYLAND PARKWAY • LAS VEGAS, NEVADA 89154 • (702) 739-3142

QAL 138:cm

August 25, 1986

Subject: UNLV-QAL Preliminary Audit of Method 6010/3050 Data Packages From Participating Laboratories

References: (1) Special Analytical Services 5-15-86 Version, "Participating Laboratories for ICP Method 6010 Study"
(2) Method 6010

The UNLV-QAL conducted an audit on the data packages from the seven participating laboratories. Although each data package had unique problems, which are described in the following sections, one problem was common to all, the timeliness of the submission. The lateness varied from 12 days to almost 1 month.

The following paragraphs discuss the problems associated with each laboratory's data package.

Laboratory P

Reference (1) page 2, Paragraph 1, specifies the requirements for performing MSA analyses. There were no MSA's performed by this laboratory.

On Form IX for Sample T DUP #1, the reported result for arsenic is given as 40 U(1:4) mg/kg. This result is meaningless because the undiluted As concentration, which was above the detection limit, should have been spiked, not diluted according to Ref. (1). Similarly this deficiency is true with respect to some of the other elements. Furthermore, according to Method 6010 (Ref. (2)) page 11, whenever a new or unusual sample matrix is encountered, a series of tests are to be performed to determine if MSA's are necessary. If the test criteria indicate MSA's are needed, then MSA's should be performed on each sample; DUP #1, DUP #2, SPK DUP #1, SPK DUP #2, as required by good laboratory practice.

Many of the values given on the Form III's for the continuing calibration blank are not within three standard deviations of the mean blank value. This is required by Ref. (2).

The true antimony value for ICV #3 reported with the liquid samples on Form II is different from the Form II values reported with the solid samples. If the standard solution used was changed, it must be indicated. If ICV #3 was used in both cases, then why are the analytical values so different (4350 vs. 8700 ug/L)?

The data package was received July 25; the deadline for receipt of the data package was July 14.

Laboratory Q

Many required forms are filled out incorrectly, and the data package is very disorganized. It is requested that the laboratory submit a complete and organized data package. It appears that the MSA requirement (given in Ref. (1)) has not been met; because of the poor data package, a full evaluation is not possible.

The data package was received on August 8, almost four weeks late.

Laboratory R

Many of the values given on the Form III's for the continuing calibration blank are not within three standard deviations of the mean blank value as required by Ref. (2).

Reference (2), page 11 states, whenever a new or unusual sample matrix is encountered, a series of tests should be performed to determine if MSA's are required. This laboratory did not perform any tests on any samples except sample SPK DUP #2 T and SPK DUP #2 W; however, MSA's were performed on almost all the samples, which is not required by the method. This may have resulted in considerably more work than required.

The data package was received on August 5, more than two weeks late.

Laboratory S

There was no analytical result reported for molybdenum on Form II (calibration verification). How was the molybdenum calibration verified?

The instrument detection limit was reported on Form III instead of calibration blank and continuing calibration blanks for which the form was designed. Form VII is for instrument detection limits. The values given on the Form III's for the continuing calibration blank should agree within three standard deviations of the mean blank value as required in Ref. (2).

Forms XI, XII, XIII are missing from the data package.

The data package was received August 11, one month late.

Laboratory T

There were no inter-element and background corrections applied to the results on Sample G according to information provided on the Form I submitted to UNLV. The laboratory should supply this information.

Many of the values given on the Form III's for the continuing calibration blank are not within three standard deviations of the mean blank value as required by Ref. (2).

Forms XI, XII, and XIII are missing.

The data package was received on August 6, almost four weeks late.

Laboratory U

The method of standard additions has not been applied to the solid sample by this laboratory as required by the criteria given in Ref. (1). For example, the MSA's was applied to only one element in each different sample, although the concentration levels reported indicate that some other elements required MSA's.

Furthermore, when MSA's were applied, they were performed only for Sample DUP #1, even though good laboratory practices require that MSA's be applied to sample DUP #2, SPK DUP #1, and SPK DUP #2.

It is necessary that the dilutions factors be given on Form IX, e.g. analytical data on diluted sample should be reported as 87100 (1:16), 1350 (1:4), etc. This was specified explicitly in the instructions.

The instrument detection limits were reported on Form III instead of calibration and continuing calibration blanks for which the form was designed. The IDL's should be reported on Form VII only.

The values given on the Form III's for the continuing calibrations blank should agree within three standard deviations of the mean blank value as required by Ref. (2).

The data package was received on July 25, almost two weeks late.

Laboratory V

This was the best organized and most complete data package received. All MSA's were performed as required. Only Form III was not filled out according to the Ref. (2). The data package was received on July 28, two weeks late.

ATTACHMENT 2

QAL REPORT 146
NOVEMBER 12, 1986

FINAL AUDIT OF THE METHOD 3050/6010 EVALUATION STUDY PARTICIPATING LABORATORY DATA PACKAGES

by

Quality Assurance Laboratory
Environmental Research Center
University of Nevada, Las Vegas
Las Vegas, Nevada 89154

Contract Number 68-01-7159

Project Officer

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OFFICE OF SOLID WASTE AND EMERGENCY RESPONSE
U. S. Environmental Protection Agency
Washington, D.C. 20460-5000

FOREWORD

This is the final audit report of the seven Method 3050/6010 participating laboratory data packages. The purpose of this report is to indicate what additional analytical work must be performed or what additional information must be furnished by the laboratories so that Method 6010 can be fully and properly evaluated.

The preliminary audit [1] of the data packages evaluated organization of the packages, completion of all the required forms, and compliance with the Method 6010 QC requirements. The data given on Form IX was also reviewed to determine whether the laboratory performed the required tests for MSA analyses.

The final audit reported here reviewed the comments and data package changes that were received in response to the preliminary audit. Laboratory compliance with the requirements for MSA analysis was checked. The number of the MSA's and the spiking that should have been performed by individual laboratories was checked using the data on Form IX and, when necessary, raw data. The laboratory MSA calculations were also spot checked.

The quality of the digestions of the soils was examined by calculating the RPD's from the duplicate results. The spike recovery and QC recovery were also calculated and checked for compliance with the Statement of Work.

SECTION 1

FINAL AUDIT OF THE DATA PACKAGES

The UNLV-QAL conducted a final audit of each data package after receiving the required information specified in our previous report (1) from three participating laboratories (Q, P, U). This audit emphasized determination of the laboratory compliance with the requirements for the method of standard additions (MSA), although the packages were also generally checked. The audit results for each laboratory are discussed below.

Laboratory Q

- The relative percent difference (RPD) for many of the elements in the samples exceeded the control limit of the 20 percent for elements with concentrations greater than ten times the detection limit.

  For example, in Sample U, the following RPD's were reported:

Element	RPD	Element	RPD
Al	71%	Fe	57%
Sb	57%	Mg	50%
Cr	50%	Zn	81%

- These large RPD's for the duplicate analyses of the same material indicate poor digestions. Although, some of the samples do not show high RPD's, the laboratory should be required to redigest the samples that have RPD's that exceed the 20 percent control limit specified in Reference 2.

Reference 2, page 1, states that whenever the concentration of any of the 23 elements in the digest exceeds the calibration range, the sample must be diluted to bring that element within the calibration range. This solution must then be diluted 1:4 and analyzed to determine if MSA is needed.

- This laboratory serial diluted the spike or duplicate spike when the serial dilution of the sample was outside the accepted limits, thus eliminating the need for an MSA for that sample. It is suggested that the laboratory perform serial dilutions on each sample; i.e., DUP #1, DUP #2, SPK #1, and SPK #2, and perform MSA's on all the samples that demonstrate the need for it.

- The chromium concentration was out of calibration in Sample U after 1:100 dilution. When the sample was diluted 1:400, the concentration was brought into the calibration range. However, the 1:4 dilution test of the diluted sample for MSA was not performed.

Laboratory P

- The reported result for nickel on Form IX for Sample T is given as 19 mg/kg; it was tested for method of standard additions. However, for Sample U, the nickel concentration is reported as 63u. This lab reported their detection limit as 31 ppb. There are contradictions here. If the 19 mg/kg for nickel is measurable for Sample T, why is 63 mg/kg not measurable in Sample U? Therefore, the results for nickel are unusable for the Method 6010 evaluations. An explanation for these apparent contradictions is required.

- This lab also selected a narrow calibration range and diluted some of their samples as much as 1:4000. This removed (by dilution) much of the interferences in the sample. This procedure may be legal, but does not satisfy the requirements of the Method 6010 Statement of Work. No other laboratory used this approach to avoid running MSA's. An explanation for the reason why a narrow calibration range was chosen is required.

- The RPD's for copper in Sample X and for cadmium in Sample Y exceeded the 20 percent control limit. It is requested that the laboratory submit an explanation for either the poor data or their failure to run MSA's for these elements.

Laboratory U

- For Samples U,V,W,X,Y,Z (Form IX), the serial dilution test shows that the concentration of the iron was not in the calibration range. Therefore, this laboratory should have diluted the sample until the concentration of the iron was in the calibration range. They then should have diluted the solution 1:4 to determine whether MSA for iron was needed.

- The laboratory did submit a revised Form IX, which addressed some of the problems with the initial forms. However, there is no evidence that the tests for the method of the standard additions on SPK #1 and SPK #2 were performed, in spite of their claim that this was done. This evidence must be submitted.

Laboratory V

- This laboratory performed the MSA's required except for the following elements:

Element	Sample
Ca	T DUP # 1
Ca	T SPK # 1
As	V SPK # 2
Sb	W SPK # 1
Mo	Y SPK # 2
Ba	Z SPK # 1
Se	Z SPK # 1
Mo	Z SPK # 1

An explanation for failure to run these required MSA analyses is needed.

- The concentration of aluminum in Sample T (Form IX) is out of the calibration limit, although the percentage difference for the element is less than 10 percent.

Laboratory S

- Most of the MSA's were completed by this laboratory. However, the tests for the following were not meaningful because the concentrations were out of calibration range:

Element	Sample
Mn	T
Cr	U
Fe	U
Al	U

Laboratory T

- Most of the MSA's were completed by this laboratory; however, the concentrations of calcium, magnesium, and manganese in Sample V were out of the calibration range. In addition, although the cadmium percentage difference was higher than 10 percent for X SPK #1 and X SPK #2, this laboratory did not perform any MSA's for this element in these samples. An explanation is needed for the failure to run the required MSA's for cadmium.

- MSA'S should have been performed for molybdenum in Sample Y DUP #2 and for arsenic in Sample H. This laboratory spiked the sample instead.

Laboratory R

- This lab performed MSA's on almost all the samples.

SECTION 2

SUMMARY

The Method 6010/3050 statement of work [3] was followed by four laboratories (S, V, T, and R). Laboratory R performed MSA's for almost all the elements in all the samples, in spite of the fact that this might not have been necessary. Laboratory Q should redigest some of the soil samples and rerun all the soil samples for the MSA's. Laboratory U claimed that they tested all the samples for MSA's, but has supplied no evidence to confirm this claim. Laboratory P did not follow the Method 6010 statement of work [3].

REFERENCES

1. "UNLV-QAL Preliminary Audit of Method 6010/3050 data packages from Participating Laboratories"; UNLV-QAL Report QAL-138 of August 25, 1986.
2. Method 6010 Statement of Work.
3. Special Analytical Services 5-15-86 Version, "Participating Laboratories for ICP Method 6010 Study."

APPENDIX H
STATISTICAL SUMMARY

STATISTICAL ANALYSIS

The objectives of the statistical analysis are (i) to evaluate the contributions of digestion variance and instrument variance to the overall analytical variance, (ii) to determine whether the data from the study indicates that all laboratories are using essentially the same procedure (i.e., are interpreting and following instructions in the same way), and (iii) to investigate whether the precision of the measurements of elements are independent of the concentrations of other elements in the performance evaluation materials (PEM's). The contributions of digestion and instrument to measurement variability is determined by variance components analysis. Failure of laboratories to use the same analytical procedure may be detected in large between-laboratory variances or in an uneven distribution of outlier measurements among laboratories. The precision of the measurement of an element is given in terms of its variance, and if the variances are not homogeneous over PEM's, this would indicate a dependence of precision of measurements of the element on the composition of the PEM.

To meet the goals stated above, the statistical analysis will identify and remove outliers in the data and will estimate variances that are due to differences between laboratories in instruments and instrument operating procedures, differences between laboratories in digestion procedures, and differences within laboratories in digestion and instrument procedures. The two sets of data investigated in this variance-components analysis are the set of measurements on the Method 6010 PEM's (spiked bulk digests, liquids) and the set of paired-replicate measurements on the spiked Method 3050/6010 PEM's (solids). Since the concentrations of the 23 measured elements in these PEM's are well above instrument detection limits, reported ND (not detected) measurements were treated as outliers and removed from the data set. The first step in the statistical analysis of the remaining data was a logarithmic transformation of the data to stabilize variances relative to changes in mean concentrations and to make the distributions more symmetric. Next, outlier tests were performed. Sets of k outliers were tested with the test statistic

$$T = \left|[x_{(1)} + \cdots + x_{(k)} - k\bar{x}]/s\right|$$

where s is the usual sample standard deviation, and $x_{(i)}$ represents the ith largest (smallest) observation, in a sample of n normally distributed observations, if one is testing for outliers on the right (left). Here an observation x is the log-transformed measurement of an element concentration in a particular PEM obtained by a participating laboratory, and n is the number of participating laboratories from which non-ND measurements of the element concentration are available. A test of the outlier-pair $x_{(1)}$, $x_{(n)}$, based on the test statistic

$$T_2 = [x_{(n)} - x_{(1)}]/s$$

where $x_{(1)}$ is the smallest observation, and $x_{(n)}$ is the largest observation, was also employed. Critical values for these tests are given in Tables VIIb, IXa, and XIa of Barnett and Lewis (1978). Henceforth, only measurements detected by these tests will be called "outliers" in order to distinguish them from ND's. If just a few of the participating laboratories have most of the ND and outlier results, one might reasonably conclude that their procedures in doing the analyses are different from those used by the other laboratories.

After removal of ND's and outliers, the basic model for the transformed measurements is

(i) for Method 6010 PEM's (spiked bulk digests),

$$Y_{ijk} = \mu_{Lik} + L_{ijk} + \epsilon_{ijk}$$

and (ii) for spiked Method 3050/6010 PEM's (solids),

$$Y_{ijkm} = \mu_{Sik} + L_{ijk} + B_{ijk} + D_{ijkm} + \epsilon_{ijkm}$$

where i is the PEM index (i=1,...7), j is the laboratory index (j=1,...,8, for Method 6010 PEM's, and j=1,...,9, for spiked Method 3050/6010 PEM's), k is the element index (k=1,...,23), and m is the PEM (replicate) sample index (m=1,2), μ is the mean, L_{ijk} is the deviation from the mean caused by the particular characteristics of laboratory j in the application of Method 6010 to the measurement of element k in PEM i, B_{ijk} is the deviation from the mean in the measurement of element k caused by performing the digestion of PEM i in laboratory j, D_{ijkm} is the deviation caused by within-laboratory variation in digestion of sample m of PEM i within laboratory j, and ϵ_{ijk} and ϵ_{ijkm} are the analytic errors. The L's, B's, D's, and ϵ's are considered to be independent normally distributed random variables with common mean zero, and variances $V(L_{ijk}) = \sigma_{Lik}^2$, $V(B_{ijk}) = \sigma_{Bik}^2$, $V(D_{ijkm}) = \sigma_{Dik}^2$, and $V(\epsilon_{ijk}) = V(\epsilon_{ijkm}) = \sigma_{Eik}^2$. One can think of σ_{Lik}^2 and σ_{Eik}^2 as the between- and within-laboratory variance components associated with Method 6010, and σ_{Bik}^2 and σ_{Dik}^2 as the corresponding variance components associated with the Method 3050 digestion procedure. Now with the model for Method 6010 PEM's, the sample variance s_{1ik}^2 over laboratories of transformed measurements on an element k in a Method 6010 PEM has expectation,

$$E(s_{1ik}^2) = E\{\Sigma(Y_{ijk} - \bar{Y}_{ik})^2/(n-1)\} = \sigma_{Lik}^2 + \sigma_{Eik}^2$$

If one is willing to assume that $\sigma_{Lik}^2 = \sigma_{Lk}^2$ and $\sigma_{Eik}^2 = \sigma_{Ek}^2$ (i.e., the variances are the same for all PEM's), then the variances s_{1ik}^2 may be averaged (pooled) over the seven PEM's to obtain the unbiased estimator s_{2k}^2 of $(\sigma_{Lk}^2 + \sigma_{Ek}^2)$. If the variances are not homogeneous over PEM's, this might be interpreted as an indication that the performance of the Method 6010 analysis for element k may be affected by the levels of concentrations of other elements in the PEM's.

For the measurements on the spiked Method 3050/6010 PEM's, two variance estimators may be obtained. The first (between digests) variance estimator is

$$s_{3ik}^2 = \Sigma_j(Y_{ijk1} - Y_{ijk2})^2/2n$$

which is an unbiased estimator of $(\sigma_{Dik}^2 + \sigma_{Eik}^2)$.

The second,

$$s_{4ik}^2 = 2\Sigma_j(\bar{Y}_{ijk} - \bar{Y}_{ik})^2/(n-1),$$

is an unbiased estimator of

$$2\sigma_{Lik}^2 + 2\sigma_{Bik}^2 + \sigma_{Dik}^2 + \sigma_{Eik}^2.$$

If the variances are homogeneous over PEM's then one may pool each of these estimators over PEM's to obtain unbiased estimators s_{5k}^2 and s_{6k}^2 of $(\sigma_{Dk}^2 + \sigma_{Ek}^2)$ and $(2\sigma_{Lk}^2 + 2\sigma_{Bk}^2 + \sigma_{Dk}^2 + \sigma_{Ek}^2)$, respectively. The variance sum $(\sigma_{Dk}^2 + \sigma_{Ek}^2)$ estimated by s_{5k}^2 is the "total within-laboratory variance." Similarly, $(\sigma_{Lk}^2 + \sigma_{Bk}^2)$, the "total between-laboratory variance," is estimated by $[(s_{6k}^2 - s_{5k}^2)/2]$. Also, s_{2k}^2 and $[(s_{6k}^2 - s_{5k}^2 - 2s_{2k}^2)/2]$ are unbiased estimators of the "total ICP (Method 6010) variance," $(\sigma_{Lk}^2 + \sigma_{Ek}^2)$, and the "total digestion variance," $(\sigma_{Bk}^2 + \sigma_{Dk}^2)$, respectively.

The test statistic used to test for homogeneity of variances is

$$Q = \delta \ln(s_{qk}^2) - \Sigma\delta_i \ln(s_{qik}^2) \qquad (q=1,3,4)$$

where δ_i is the number of degrees of freedom associated with the estimate s_{qik}^2 and $\delta = \Sigma\delta_i$. This test associated with this statistic is commonly called Bartlett's test. The test is very sensitive to the assumption that the data are normally distributed and typically gives a higher percentage of false positives than is predicted under the normal distribution hypothesis. For this reason, a critical value, 35, was chosen that was well above the typical 5 and 1 percentiles suggested under the normal hypothesis. For the tests performed on this data, there was a virtual continuum of test statistic values up to 35, and then large jumps up to larger values.

STATISTICAL EVALUATION OF DATA FROM METHOD 6010 PEM's

After removal of 28 ND's and the log (base 10) transformation of the remaining concentration measurements of elements in the Method 6010 PEM's, a search for outliers was performed using the test statistics T and T_2 mentioned earlier. A 5 percent significance level was used for both tests. The result of the outlier testing was the removal of 80 measurements from the 161 (=23x7) element-by-sample combinations of eight measurements each. The individual outliers and ND's are shown in Table 7 in the body of the report. Table 1 shows how the outliers were distributed across laboratories and the Method 6010 PEM's, and Table 2 shows how they were distributed across laboratories and elements. Of particular interest here is the unequal distribution of outliers across laboratories, which may be indicative of variations in actual procedures used in the Method 6010 analyses. Laboratory C had three ND's and two outliers (on the left) in measuring Mo; and, for the remaining two Method 6010 PEM's, its measurements for Mo were below the interlaboratory averages.

After removal of outliers, sample variances, s_{1ik}^2, across laboratories were calculated for each Method 6010 PEM i and each metal k. If the test statistic Q was less than 35, the variances were considered homogeneous, and they were pooled to obtain s_{2k}^2 the unbiased estimate of the sum of interlaboratory and analytical variances, $\sigma_{Lk}^2 + \sigma_{Ek}^2$, for element k. The variances for 17 elements were found to be homogeneous across Method 6010 PEM's, while the variances were found to be heterogeneous for the other six elements (Sb, As, Be, Cr, V, and Na). For five of these six

TABLE 1. DISTRIBUTION OF OUTLIERS* BY LABORATORY AND METHOD 6010 PEM

6010	Laboratory								
PEM	A	B	C	E	F	G	H	I	Total
HW 1			2		1				3
River Sediment	2	2	5	1	2	2		3	17
Fly Ash	1	6	6	4		7	2	6	32
Estuarine Sed.		2	3	3	1	1	2	1	13
Industrial		1	4	2		3	2		12
Electroplating	1	3	6	6	1			1	18
Mine Tailing		3	2	3	1	1	1	2	13
Total	4	17	28	19	6	14	7	13	108

* Includes ND's (Not Detecteds)

TABLE 2. DISTRIBUTION OF OUTLIERS* IN METHOD 6010 PEM DATA BY LABORATORY AND ELEMENT

	Laboratory								
Element	A	B	C	E	F	G	H	I	Total
Al		2	1	1			1		5
Sb		4						1	5
As		1	1	2					4
Be			1					1	2
Cd		1	1	3				1	6
Ca				2		1			3
Cr			1	2					3
Co				1		1		1	3
Cu					3		1	3	7
Fe				1		1			2
Pb		1	4	1		1	1		8
Mg						1			1
Mn	2						1		3
Mo			5			1			6
Ni		2	2			1		1	6
Se	1	2	5			1		1	10
Ag			1	1	3	1	1	1	8
Tl	1	1	1	4		1		2	10
V		3	3			1		1	8
Zn			1	1		3			5
Ba									0
Na			1				1		2
K							1		1
Total	4	17	28	19	6	14	7	13	108

* Includes ND's (Not Detecteds)

elements, the maximum variance, s_{1ik}^2, occurred for Fly Ash. The elements Be and V have homogeneous sets of variances for subsets of six of the seven PEM's. The estimates for total Method 6010 (ICP) variance for the 21 elements are given in Table 3.

STATISTICAL ANALYSIS OF DATA FROM SPIKED METHOD 3050/6010 PEM's

This statistical analysis follows a similar pattern to that which was employed on the data from the Method 6010 PEM's. The data and the outliers and ND's that were removed from the data are shown in Table 10 in the body of the report. Tables 4 and 5 of this appendix give the distribution over laboratories, spiked Method 3050/6010 PEM's, and elements, of replicate pairs of sample measurements that contain ND's or outliers. These tables should be compared with Tables 1 and 2 which give similar results for data from the Method 6010 PEM's. Fewer outliers and ND's were found in the spiked Method 3050/6010 PEM data than in the data from the Method 6010 PEM's. However, Laboratory C was found to have trouble measuring Mo in both data sets. Tables 6 and 7 give the pooled variance estimates s_{5k}^2 and s_{6k}^2. The sets of variance estimates s_{3ik}^2, that were pooled to obtain s_{5k}^2 values in Table 6, were quite heterogeneous. For this reason, median s_{3ik}^2 values across the seven PEM's were included in Table 6 to show a different type of average within-laboratory variance estimate. Table 8 shows estimates of the variances attributable to within-laboratory variability, between-laboratory variability, Method 6010 performance variability, and Method 3050 digestion variability. Columns A and B in Table 8 indicate that between-laboratory variability exists and makes a considerably greater contribution to total variance than does within-laboratory variability. A comparison of Columns C and D indicates no such dominance relationship between the Method 6010 procedure variability and the Method 3050 digestion procedure

TABLE 3. POOLED VARIANCE ESTIMATES s_{2k}^2 BASED ON METHOD 6010 PEM DATA

Element*	Variance Estimate	Degrees of Freedom
Al	0.0030	44
Cd	0.0014	43
Ca	0.0012	46
Co	0.0023	46
Cu	0.0014	42
Fe	0.0012	47
Pb	0.0025	41
Mg	0.0031	48
Mn	0.0023	46
Mo	0.0159	43
Ni	0.0015	43
Se	0.0033	39
Ag	0.0268	41
Tl	0.0130	40
Zn	0.0023	44
Ba	0.0018	49
K	0.0012	48
Be[1]	0.0009	40
V[1]	0.0025	37
As[2]	0.0029	
Sb[2]	0.0014	
Cr[2]	0.0010	
Na[2]	0.0023	

[1] Estimated variances from the seven samples failed to satisfy the homogeneity test. Pooled variance shown was obtained after removal of one outlier which left samples whose variance estimates satisfy the homogeneity test.

[2] Variance estimates are medians of the seven sample s_{1ik}^2 values because of the heterogeneity of the variances for these elements could not be eliminated by the removal of one outlier variance estimate.

TABLE 4. DISTRIBUTION OF OUTLIERS* BY LABORATORY AND SPIKED METHOD 3050/6010 PEM

3050/6010	Laboratory									
PEM	A	B	C	D	E	F	G	H	I	Total
HW 1		1	2		3	5		2		13
River Sediment		1	3	1	1	1	2	1	3	13
Fly Ash	1	1	1			2		1		6
Estuarine Sed.		13	1		2		1	1		18
Industrial		7	1	1			1	1		11
Electroplating		2	1	4	1	1	4	1		14
Mine Tailing				1	2	1	3	1	2	10
Total	1	25	9	7	9	10	11	8	5	85

* Includes ND's (Not Detecteds)

TABLE 5. DISTRIBUTION OF OUTLIERS* IN THE SPIKED METHOD 3050/6010 METHOD PEM DATA BY LABORATORY AND ELEMENT

	Laboratory									
Element	A	B	C	D	E	F	G	H	I	Total
Al		1								1
Sb						1	1			2
As		1								1
Be				1						1
Cd						2				2
Ca		2				1				3
Cr		1			3				1	5
Co		1				1	1			3
Cu		1		1				2	1	5
Fe		1								1
Pb		1				1	1			3
Mg		2								2
Mn	1	3								4
Mo		1	6			1				8
Ni		1		1	2	1			1	6
Se		1	2			1	1		1	6
Ag		1			2		3	6		12
Tl		2		2	1					5
V		2	1				1		1	5
Zn					1					1
Ba				1			1			2
Na		3			1					4
K				1		1	1			3
Total	1	25	9	7	9	10	11	8	5	85

* Includes ND's (Not Detecteds)

TABLE 6. POOLED VARIANCE ESTIMATES[a] s_{5k}^2 OF WITHIN-LABORATORY VARIANCE BASED ON SPIKED 3050/6010 PEM DATA

Element	Variance Estimate	Median of s_{3ik}^2	Degrees of Freedom
Al	0.0008	0.0006	62
Sb	0.0027*	0.0009	61
As	0.0008	0.0004	62
Be	0.0013*	0.0015	62
Cd	0.0011	0.0008	61
Ca	0.0005	0.0003	60
Cr	0.0003	0.0001	58
Co	0.0007	0.0005	60
Cu	0.0006*	0.0002	51
Fe	0.0013	0.0006	62
Pb	0.0004	0.0002	60
Mg	0.0004	0.0003	61
Mn	0.0008*	0.0003	59
Mo	0.0008	0.0008	55
Ni	0.0012*	0.0003	58
Se	0.0004	0.0002	57
Ag	0.0059*	0.0037	51
Tl	0.0079*	0.0010	58
V	0.0025*	0.0023	57
Zn	0.0011*	0.0006	62
Ba	0.0024*	0.0024	61
Na	0.0004*	0.0001	59
K	0.0011*	0.0005	60

* Failed homogeneity test.

[a] s_{5k}^2 estimates $(\sigma_{Dk}^2 + \sigma_{Ek}^2)$ and is a weighted mean of s_{3ik}^2 values.

TABLE 7. POOLED VARIANCE ESTIMATES[a] s_{6k}^2 BASED ON THE SPIKED METHOD 3050/6010 PEM DATA

Element	Variance Estimate	Degrees of Freedom
Al	0.0138	55
Sb	0.0880	54
As	0.0155	55
Be	0.0059	55
Cd	0.0094	54
Ca	0.0043	53
Cr	0.0075	51
Co	0.0111	53
Cu	0.0068	51
Fe	0.0210	55
Pb	0.0072	52
Mg	0.0043	54
Mn	0.0059	52
Mo	0.0238	48
Ni	0.0100	50
Se	0.0070	50
Ag[1]	0.2237 (0.0191)	44
Tl	0.0335	51
V	0.0182	51
Zn	0.0072	55
Ba	0.0074	54
Na	0.0178	52
K	0.0098	53

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[1] Removal of largest of seven sample variances left a homogeneous set whose pooled value is in the parentheses.

[a] s_{6k}^2 estimates $(2\sigma_{Lk}^2 + 2\sigma_{Bk}^2 + \sigma_{Dk}^2 + \sigma_{Ek}^2)$.

TABLE 8. POOLED VARIANCE ESTIMATES OF VARIANCE COMPONENTS BASED ON METHOD 6010 PEM AND SPIKED METHOD 3050/6010 PEM DATA

	ESTIMATES				
Elements	Total Within Lab. Var. A*	Total Between Lab. Var. B*	Total ICP Variance C*	Total Digestion Variance D*	Total Variance E*
Al	0.0008	0.0065	0.0030	0.0043	0.0073
Cd	0.0011	0.0042	0.0014	0.0039	0.0053
Ca	0.0005	0.0019	0.0012	0.0012	0.0024
Co	0.0007	0.0052	0.0023	0.0036	0.0059
Cu	0.0006	0.0031	0.0014	0.0023	0.0037
Fe	0.0013	0.0099	0.0012	0.0100	0.0112
Pb	0.0004	0.0034	0.0025	0.0013	0.0038
Mg	0.0004	0.0019	0.0031	0.0000[a]	0.0024
Mn	0.0008	0.0026	0.0023	0.0011	0.0034
Mo	0.0008	0.0115	0.0159	0.0000[a]	0.0147
Ni	0.0012	0.0044	0.0015	0.0041	0.0056
Se	0.0004	0.0033	0.0033	0.0004	0.0037
Tl	0.0079	0.0128	0.0130	0.0077	0.0207
Zn	0.0011	0.0031	0.0023	0.0019	0.0042
Ba	0.0024	0.0025	0.0018	0.0031	0.0049
K	0.0011	0.0044	0.0012	0.0043	0.0055
Be[1]	0.0013	0.0023	0.0009	0.0027	0.0036
V[1]	0.0025	0.0079	0.0025	0.0079	0.0104
Sb[2]	0.0027	0.0426	0.0014	0.0439	0.0453
As[2]	0.0008	0.0073	0.0029	0.0053	0.0082
Cr[2]	0.0003	0.0036	0.0010	0.0029	0.0039
Na[2]	0.0004	0.0087	0.0023	0.0068	0.0091
Ag[3]	0.0059	0.0191	0.0287	0.0000[a]	0.0250
Median[4]:	0.0008	0.0038	0.0023	0.0027	0.0051

(continued)

TABLE 8 (continued)

* Column A gives values of s_{5k}^2 (from Table 6) which estimate ($\sigma_{Dk}^2 + \sigma_{Ek}^2$) under the model for solids.

Column B gives values of $\lfloor(s_{6k}^2 - s_{5k}^2)/2\rfloor$ which estimate ($\sigma_{Lk}^2 + \sigma_{Bk}^2$) under the model for solids.

Column C gives values of s_{2k}^2 (from Table 3) which estimate ($\sigma_{Lk}^2 + \sigma_{Ek}^2$), the "total Method 6010 (ICP) variance," under the model for liquids.

Column D gives values of $\lfloor(s_{6k}^2 + s_{5k}^2 - 2s_{2k}^2)/2\rfloor$ which estimate ($\sigma_{Bk}^2 + \sigma_{Dk}^2$), the "total digestion variance." Column A plus Column B minus Column C.

Column E gives values of $\lfloor(s_{5k}^2 + s_{6k}^2)/2\rfloor$ which estimate the "total variance," ($\sigma_{Lk}^2 + \sigma_{Bk}^2 + \sigma_{Dk}^2 + \sigma_{Ek}^2$). Column A plus Column C.

[1] Pooled variance estimate in Column C is based on six PEMs whose set of variance estimates satisfy the homogeneity test.

[2] Variance estimates in Column C are medians of the 7 sample s_{1ik}^2 values because of the heterogeneity of the variances for these elements.

[3] Pooled variance estimate in Column B is based on six PEM's whose set of variance estimates satisfy homogeneity test.

[4] Medians are over variance estimates for first 16 listed elements. Corresponding medians over all 23 elements are 0.0008, 0.0044, 0.0023, 0.0031, and 0.0056.

[a] Estimate set to zero because the difference used in calculating the variance estimate gave a negative value.

variability. The medians over the first 16 elements shown at the bottom of Table 8 tend to indicate that overall the two procedures are making approximately equal contributions to the total error variance of the measurements. The percentage contributions of Method 6010 and Method 3050 digestion to the total variance are given in Table 9. The percentage contributions of between-laboratory variance and within-laboratory variance to total variance is shown in a similar way in Table 10.

REFERENCE

Barnett, V., and T. Lewis. Outliers in Statistical Data. John Wiley & Sons, New York, 1978. 365 pp.

TABLE 9. ESTIMATED PERCENTAGE CONTRIBUTIONS OF METHOD 6010 ICP VARIANCE AND METHOD 3050 DIGESTION VARIANCE TO TOTAL VARIANCE

Elements	6010 ICP	3050 Digestion
Al	41	59
Cd	26	74
Ca	50	50
Co	39	61
Cu	38	62
Fe	11	89
Pb	66	34
Mg	100	0 [a]
Mn	68	32
Mo	100	0 [a]
Ni	27	73
Se	89	11
Tl	63	37
Zn	55	45
Ba	37	63
K	22	78
Be[1]	25	75
V[1]	24	76
Sb[2]	3	97
As[2]	35	65
Cr[2]	26	74
Na[2]	25	75
Ag[3]	100	0 [a]
Median[4]:	45.5	54.5

[1,2,3,4, a] See correspondingly identified footnotes in Table 8. Over all 23 elements the medians are 38 and 62

TABLE 10. ESTIMATED PERCENTAGE CONTRIBUTIONS OF BETWEEN-LABORATORY AND WITHIN-LABORATORY VARIANCES TO TOTAL VARIANCE

Elements	Within	Between
Al	11	89
Cd	21	79
Ca	21	79
Co	12	88
Cu	16	74
Fe	12	88
Pb	11	89
Mg	17	83
Mn	24	76
Mo	5	95
Ni	21	79
Se	11	89
Tl	38	62
Zn	26	74
Ba	49	51
K	20	80
Be[1]	36	64
V[1]	79	21
Sb[2]	6	94
As[2]	10	90
Cr[2]	8	92
Na[2]	4	96
Ag[3]	24	76
Median[4]:	18.5	82.5

[1,2,3] See correspondingly numbered footnotes in Table 8. Over all 23 elements the medians are 17 and 83.